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OUTLINES

OF

CHEMICAL ANALYSIS,

PREPARED FOR

THE CHEMICAL LABORATORY AT GIESSEN.

BY

DR. HEINRICH WILL,

PROFESSOR OF EXPERIMENTAL CHEMISTRY IN THE UNIVERSITY
AT GIESSEN.

TRANSLATED FROM THE THIRD GERMAN EDITION,

BY

DANIEL BREED, M.D.
OF THE U. S. PATENT OFFICE, LATE OF THE LABORATORIES OF LIEBIG,
LÖWIG, AND WILL,

AND

LEWIS H. STEINER, M.A., M.D.
PROFESSOR OF CHEMISTRY NAT. MED. COLLEGE.

BOSTON AND CAMBRIDGE:
JAMES MUNROE AND COMPANY.
1855.

CAMBRIDGE:
ALLEN AND FARNHAM, PRINTERS.

TO

PROFESSOR E. N. HORSFORD,

OF THE LAWRENCE SCIENTIFIC SCHOOL,

THIS TRANSLATION

IS RESPECTFULLY DEDICATED

BY

THE TRANSLATORS

TRANSLATORS' PREFACE.

In view of the increasing attention paid throughout our land to the subject of Chemistry, more especially as applied to the arts and sciences, the translators of the third German edition of Will's Outlines of Chemical Analysis feel that they are placing in the hands of the student a most invaluable guide in analytical operations. It embraces the results of the experience of many years in the laboratory of Giessen, so celebrated all over the scientific world,—especially for its accuracy in the various branches of analysis, and contains in a compendious form, the processes adopted by Professor Liebig, as well as those by the author—for many years assistant, and at present successor to that great chemist. The student and the advanced analyst will find here those simple rules for conducting analyses which will aid them in arriving at the most reliable results, whilst they leave them free to exercise that judgment so indispensably requisite in every chemical process.

The place proposed to be filled by this work is not now occupied by any other. The large treatise of Rosé is wholly unsuited to the *beginner;* it is a work for the study rather than for the laboratory, and while it is a monument of the labor and research of its author, and is authority of the highest character as a reference, it is necessary to have some book better suited to the beginner, and at the same time, available to the advanced student.

The first German edition was eagerly embraced by chemical students throughout Germany; it was translated by Professor Hoffman, for the use of the Royal College of Chemistry in London, and an American edition, prepared under the auspices of Professor Horsford, of Cambridge, Massachusetts, was used as a text-book by the students of the Lawrence Scientific School. Since the publication of that edition, chemical science has made great advancement, and many improvements and alterations have been introduced in analysis, which the author has incorporated in this edition of his work. Believing that the transference of these to the English would be a grateful task, and one sure to benefit scientific research in this country, the author was written to by one of the translators, who, in reply, writes: * * * * "Should you carry out your intention of taking the translation in hand, which will give me much pleasure, I would advise you to take, as the basis of your translation, the third German edition, which is improved in many material points. * * * * For fear you cannot yet find it in the United States, I have ordered my bookseller here to send you, by a safe conveyance, a copy of this edition, with the tables. I wish you a speedy reception of the same, and hope that your labor may meet that success which you expect from it."

In rendering the ideas of the author into English, the translators have endeavored to be as literal as the idioms of the two languages would permit. The nomenclature has been made to accord with the standard authorities of the day, and is substantially the same as that adopted by one of the translators in his edition of Löwig's Organic Chemistry. Prefixed is a short introduction, explaining the principal manipulations required in analysis, which it is hoped will prove useful to such as are not in a situation to avail themselves of practical instruction.

Washington, D. C., Nov. 1854.

PREFACE

TO THE FIRST EDITION.

A PRACTICAL course in chemical analysis is always preceded by a theoretical one, in which the practical chemist acquires the preliminary scientific knowledge necessary for the work, and on this account, in an introduction to chemical analysis — intended, as the present, for use in the laboratory — every thing is omitted which is not directly connected with analysis itself.

If we consider the understanding of the scientific principles on which the methods of analysis depend, and the improvement of the judgment and the powers of reflection, as the chief objects of instruction in a chemical laboratory, then it is self-evident that the introductory treatises, which are designed for self-instruction, are not fitted for use in the laboratory. They presuppose, in the nature of the case, no chemical knowledge, on which account a number of subjects must be treated — such as the method of exhibiting reagents — which the practical chemist understands from their mere mention, and finds in every text-book; or a knowledge of which — (such as apparatus and chemical utensils) — he acquires on his entrance into the laboratory. Of these books those are justly considered best which allow the acquisition of methods of analysis without the assistance of a teacher, and hence all the other advantages of instruction are sacrificed in favor of the mechanical routine or the successive series of operations, which lead to the sure discovery of separate substances or to their separation; on this account they are prepared so as to leave as little as possible to reflection proper.

The need of an Introduction to Chemical Analysis, solely designed for use in the laboratory, has occasioned the publication of this little treatise, which has been undertaken at my suggestion by Professor H. Will, my assistant for many years; the course described in it is that which I have employed with advantage, and found reliable, for twenty-five years in this laboratory.

JUSTUS LIEBIG.

PREFACE TO THE SECOND EDITION.

THE form of the Outlines of Chemical Analysis, chosen by me, has answered well its end, for use in the laboratory — according to my own manifold experience, and also to the communications of approved teachers — so that I have essentially retained it, in this second edition. A greater extension has been given to the tabular forms in qualitative chemical analysis, as is evident from the increased number of the tables (on which account they appear separate and in larger form). I have taken, for practice in quantitative chemical analysis, a series of examples, which will make the advancing practical chemist acquainted with the most important methods of determination and separation, without on the other hand interfering with his own self-activity by a circumstantial description of these methods.

HEINRICH WILL.

Giessen, October 21, 1850.

PREFACE TO THE THIRD EDITION.

In the preparation of the third edition of the Outlines of Chemical Analysis, without altering its plan or enlarging its compass, I have endeavored, by increasing the examples for practice in quantitative and especially volumetric analysis, to increase the utility of the work in this direction. The arrangement of the tables has not been materially altered.

HEINRICH WILL.

Giessen, October, 1853.

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PART FIRST.

COMPORTMENT OF THE METALLIC OXIDES AND THEIR SALTS.

PART SECOND.

COMPORTMENT OF THE METALLOIDS AND THEIR MORE IMPORTANT COMPOUNDS.

PART THIRD.

COURSE OF QUALITATIVE CHEMICAL ANALYSIS.

PART FOURTH.

EXAMPLES FOR PRACTICE IN QUANTITATIVE ANALYSIS.

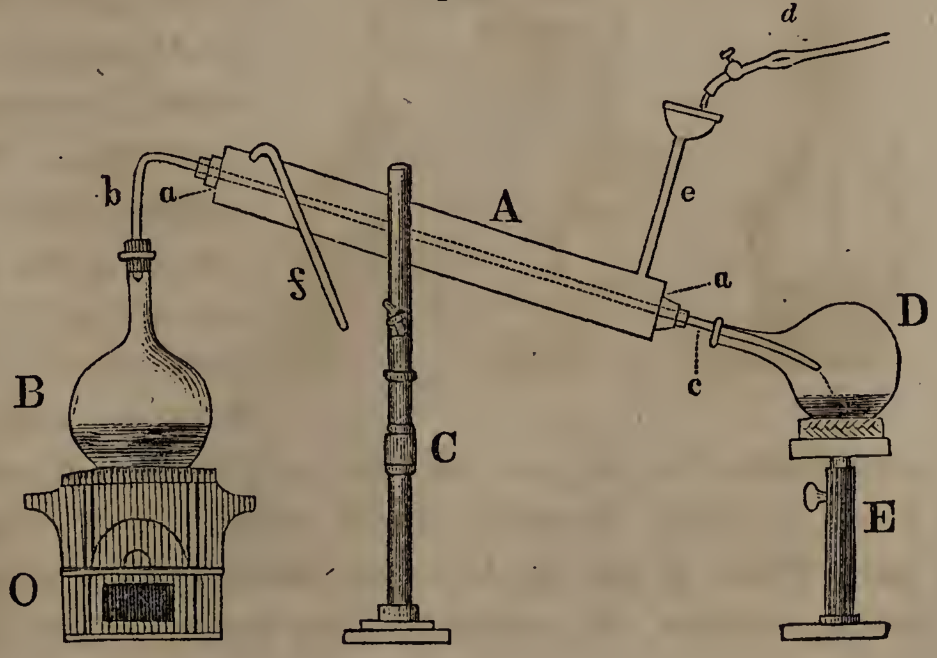
INTRODUCTION.

The German student, for whom this volume is expressly prepared, is abundantly provided with introductory works, and has ever easy access to well-furnished laboratories and the best instruction; to meet in some degree the want so often felt by the American student, especially when deprived of the advantages of laboratory instruction, the translators have prepared the following simple pages, which may aid the isolated beginner in pursuing his researches.

WATER AND DISTILLATION.

The first reagent which the private student must prepare for himself, is chemically pure water. Clean rain water, and some other very pure waters, may be rendered suitable for many laboratory purposes, by simply boiling and filtering. But it is usually better to distil water, rejecting the first eighth which goes over, and leaving a still larger quantity in the retort at the close of the distillation. The retort should always be well washed before refilling. Water thus purified should be preserved in closely stoppered stone jars. The best vessel for distilling water is a copper boiler with a tin cover, but for most purposes a glass retort (3 qts.) may be employed, (water thus distilled leaves a slight residue after evaporating to dryness,) or the distilling apparatus shown fig. 1, in which *B* is a large flask resting on a portable kitchen furnace *O*; *A* is Liebig's condenser, supported by a retort-holder *C*; *D* is also a flask used as a receiver, which may be placed upon *E*, or if necessary in a bowl of cold wa-

Fig. 1.



ter. The condenser *A* consists of a copper or tin tube through which the glass tube *a* passes, fitting water tight at the ends. The small tubes *c* and *b* are provided with corks, except at the connection with *D*. Now if cold water (put ice in the supply vessel if necessary) be allowed to flow continuously from tube *d* into the funnel tube *e*, the tin tube *A* will be filled with cold water, and the warmer water will flow out at the top by the tube *f*, whilst the vapor from flask *B*, in passing through the tube *a*, will be condensed and retained in receiver *D*.

The common tests for water supposed to be pure, are

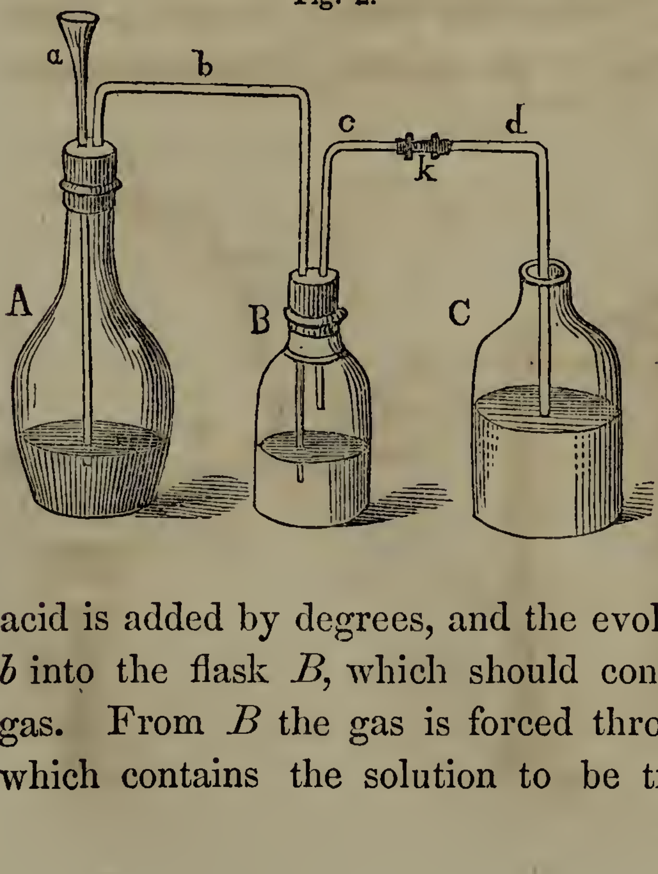
1. Evaporation to dryness.
2. Test-paper.
3. Perfectly clear lime water.
4. Solution of nitrate of silver.
5. " " chloride of barium.
6. " " oxalate of ammonia.

The first test should leave no residue, and the others should show no reaction. (A few drops of the reagent must be added to a portion of water in a clean test-tube, and held to the eye in a clear light.)

SULPHYDRIC ACID GAS.

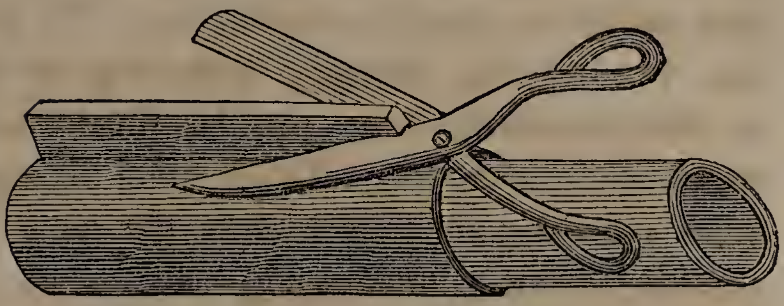
Sulphydric acid gas should be evolved at the moment of using it. For this purpose sulphide of iron is prepared, by mixing intimately five parts flowers of sulphur with eight parts iron filings, and bringing the mixture, in small portions at a time, heated to redness, into a red-hot Hessian crucible (around which, when supported on a brick in a furnace, a coal fire is built) which is covered until the whole mass glows. When cool, the sulphide of iron, in fragments of the size of a pea, is placed in a bottle *A*, fig. 2, and covered with pure water. Through funnel tube *a* concentrated sulphuric acid is added by degrees, and the evolved gas can escape only through *b* into the flask *B*, which should contain some water for washing the gas. From *B* the gas is forced through tubes *c* and *d* into flask *C*, which contains the solution to be treated. An india-rubber tube *k*,

Fig. 2.



slipped upon *c* and *d* and then tied, affords flexibility, and allows tube *d* to be removed for cleaning. This tube *k* is readily made by wrapping sheet rubber around a glass rod and then cutting it off, as is seen in fig. 3. If the joint be not completely closed by cutting, the seam may be pinched together by small forceps before slipping out the rod, (which may be moistened before being used).

Fig. 3.



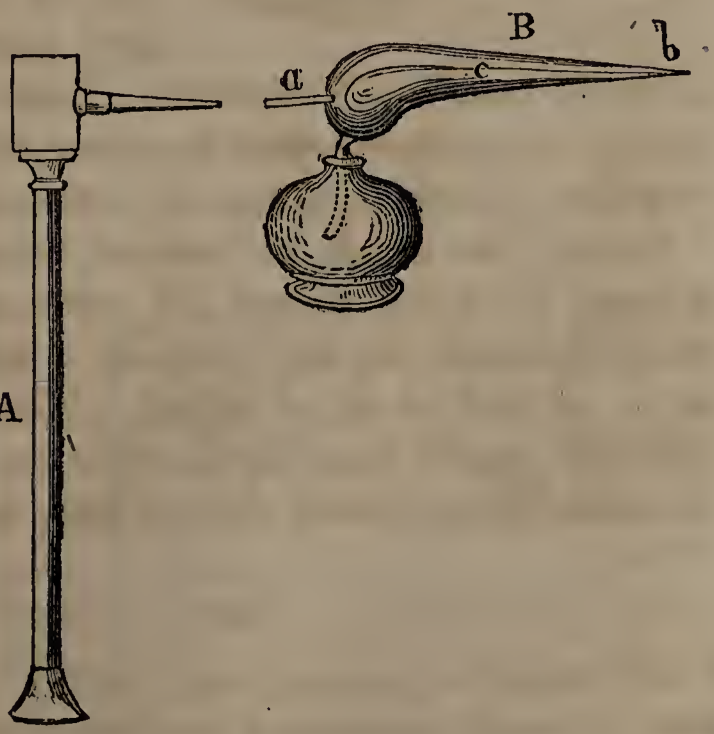
SULPHIDE OF AMMONIUM.

Sulphide of ammonium should be often freshly prepared, and preserved in a well-stoppered bottle. It is obtained by conducting sulphydric acid into aqueous ammonia until the latter absorbs no more of the gas. The apparatus, fig. 2, will serve for the purpose by the addition of a loose stopper to flask *C*, in which the aqueous ammonia is to be placed.

BLOWPIPE.

By means of the blowpipe many substances can be determined qualitatively, and some quantitatively. Our present purpose is simply to illustrate the two flames of this instrument. In the accompanying cut *A* represents a blowpipe; *a* the position of the tip when blowing, *B* the blowpipe flame, *b* the tip of the outer or oxidizing flame, *c* the inner or reducing flame. Before testing a substance with the blowpipe, it is proper to ascertain whether it be organic or inorganic. For this purpose a few particles are placed upon a slip of platinum foil (3 inches long and ¾ inch wide, and with a cork slit and slipped on

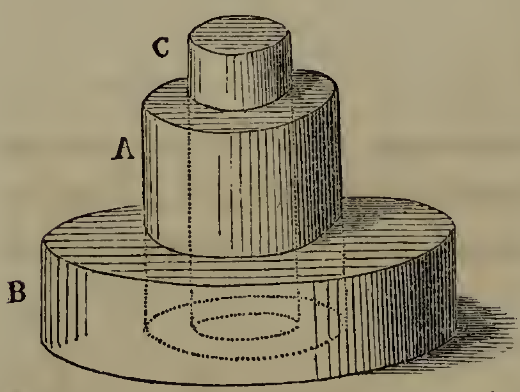
Fig. 4.



one end as a handle), and slowly heated over the flame of the alcohol lamp, carefully observing any appearance of vapor or smoke, charring, and partial or complete combustion. To increase the heat in completing this test, the blowpipe flame may be directed upon the substance, or what is usually better, against the under-side of the foil, below the substance to be tested. The gradual disappearance of a volatile metal must not be confounded with the phenomena characteristic of an organic substance undergoing combustion. Care must be taken not to heat upon platinum any easily fusible metal (e. g. bismuth, lead, silver, tin, etc.), as an alloy of the metals would thus be made, (which, in case of a platinum crucible, would be an expensive experiment). In experiments with the blowpipe, as in all his labors, the student should make a memorandum of every phenomenon at the time that it is observed, as the apparently most trifling circumstance may afterwards be found of great importance: not a single fact should be wholly trusted to even the best memory, and a negative circumstance be noted as carefully as a positive.

Minerals usually require preparation for the blowpipe, as for solution (see page 180) by pulverization. They may be broken in small pieces with a hammer and then crushed in the accompanying steel mortar, in which rim *A* is removable from bottom *B*. Pestle *C* fits the rim closely and is driven by a heavy hammer into the rim upon the mineral. If repetition of this process does not soon prepare the mineral for the blowpipe, trituration in an agate mortar may be resorted to, as is generally necessary for solution. Some minerals may be sufficiently reduced by wrapping them in strong, clean paper, and giving them a blow with a hammer, taking care not to contract any impurity.

Fig. 5.



Having pulverized the mineral, we next proceed to test it upon charcoal, (of which a piece six inches long, of close uniform texture may be selected, one end wrapped in paper, and in the other a small cavity cut half the size of a pea). Take a little of the pulverized mineral, and placing it in the cavity of the coal, slowly heat it, first with the outer, and afterward with the inner flame* of the blowpipe, noting

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* To increase the blowpipe flame, oil may be employed, or strong alcohol in which one twelfth part spirits of turpentine is dissolved.

the effects. Further results may be obtained by covering a portion of the substance with several times its bulk of carbonate of soda and heating as before. Repeat the operation, using carbonate of potassa, then a mixture of the two carbonates, then cyanide of potassium, or other reagents. After treatment of ores, a metallic button is sometimes found upon the charcoal, but if the substance disappear, without odor or fumes, metallic granules should be sought by cutting out the charcoal at the bottom of the cavity, and grinding it somewhat in an agate mortar. Then by addition of water to float off the coal, and careful decantation, small grains of metal may be found in the mortar. If these grains are not perceptible after repeated washing, the characteristic lustre of the softer metals may often be brought out by strongly rubbing the residue with the pestle, metallic streaks being left upon the mortar, or flattened grains which may be cut to show their lustre.

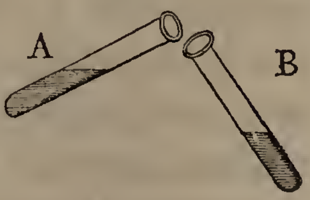
For testing substances with borax, phosphate of ammonia-soda, nitrate of cobalt, etc., to ascertain the color of the beads formed by fusion with blowpipe, a very fine platinum wire is coiled at one end as a support, and the other end may have a glass or cork handle.

SOLUTION AND CARBONIC ACID.

In qualitative analysis small quantities are usually employed, therefore the solution of solids may be most conveniently conducted in a test tube which may be readily heated over an alcohol lamp. The tube should be perfectly dry externally, and slowly warmed at first. For quantitative analysis, the solution is better conducted in a beaker-glass, or in a flask with a large mouth, the vessel being placed obliquely to prevent loss from drops ejected by the evolved gases.

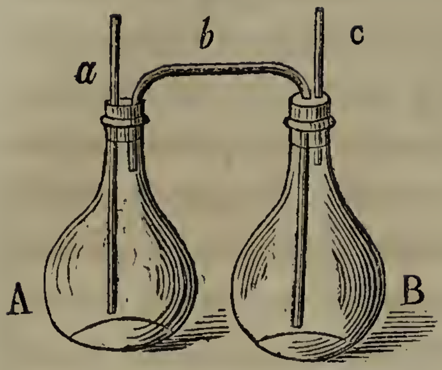
If, in dissolving a substance, a colorless and inodorous gas is evolved, the latter may be carbonic acid (167), and may be tested in the following simple manner. — During evolution of gas in tube *A*, fig. 6, the lip of the tube may be brought upon that of tube *B*, containing clear lime water. As the gas from tube *A* flows into tube *B*, the water will become milky from formation of carbonate of lime.

Fig. 6.



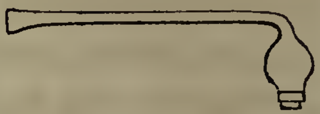
The quantitative determination of carbonic acid (see pages 167, 227) may be best conducted in Will and Fresenius' apparatus, fig. 7. *A* and *B* are thin two-ounce flasks, with corks fitting air-tight. The weighed substance is placed in flask *A* and covered with water. *B* is one third filled with concentrated sulphuric acid. Tube *a* is

Fig. 7.



closed at the top with a ball of wax, and the apparatus thus charged is weighed; now by means of suction tube fig. 8, (the hole in the cork of which fits tube *c*, fig. 7); air is drawn from flask *B* until, on removal of the mouth, a few drops of sulphuric acid are forced over into flask *A*. When the evolution of gas ceases, repeat the suction so long as additional portions of sulphuric acid liberate carbonic acid. Finally the ball of wax is removed, and suction is continued so long (from five to ten minutes) as the sweet taste of carbonic acid is perceived. The apparatus is cooled (replacing wax ball) and weighed. The loss is the weight of carbonic acid expelled.

Fig. 8.



PRECIPITATION AND DECANTATION.

Many circumstances are to be considered in deciding whether a precipitate will be produced with a given reagent, as temperature, concentration, or dilution, the presence of some disturbing agent, or absence of a substance which might favor the action by the influence of some affinity. Therefore a single trial should not satisfy the student, but the experiment should be varied, especially should resort be had to *heat*, *agitation*, and *time*.

The beaker and test tube serve best for precipitation, the liquid in the former being agitated by a glass rod. In quantitative experiments, after forming a precipitate it should be left to subside, and then a few drops more of the precipitant added (see p. 185), to ascertain whether any additional precipitate may be produced, (care should be taken not to dissolve the precipitate by excess of the precipitant). When the precipitation is complete, the subsidence of the precipitate often allows the mother-liquor to be removed by decantation. Precipitates of baryta, for example, may be readily separated and washed without filtration. To avoid spilling in decanting, a portion of the lip of the vessel should be smeared internally and externally, with tallow, and then this portion brought against a glass rod held obliquely, when the liquid will flow gently down the rod without danger of waste.

FILTRATION.

Precipitates are generally separated from the mother-liquor by filtration, as shown in fig. 8½, through paper expressly prepared for the purpose, (Swedish is best, but a cheaper article is sufficient for most purposes); the paper is cut in a circular form, folded in the shape of a quadrant, the pointed part placed deep in a glass funnel, and one of the folds spread back so that the paper completely lines the glass, though it must not quite reach the top. When nearly fitted, the paper is moistened by a jet of water to cause it to adhere to the glass. If a precipitate subside, the supernatant liquid should first be run through the filter (to accelerate filtration), and the precipitate be then poured upon the filter, the last particles (in quantitative analysis) being washed from the vessel by a small jet of water. When the liquid is drained off, the precipitate is washed down from the sides of the filter by a stream of water from the jet-flask, fig. 9, the mouth being placed upon tube *a* to force a jet from point *b* by a gentle blast. This washing must be continued until all the mother-liquor is removed (testing on platinum foil for residue, if water only has been employed in washing).

Fig. 8½.

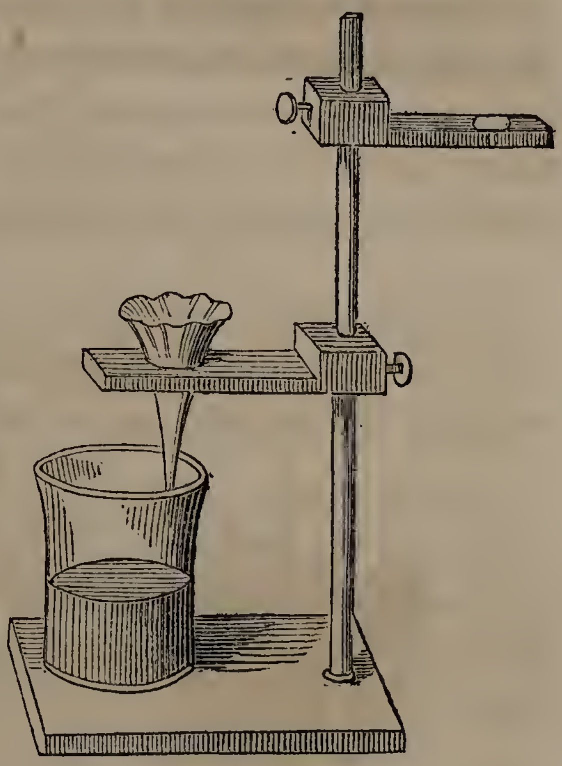
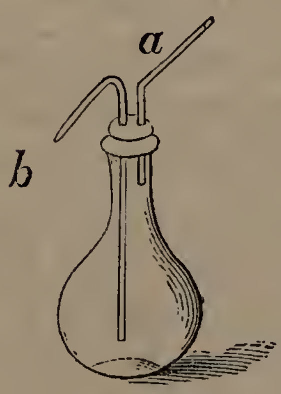


Fig. 9.



EVAPORATION.

After filtration, the mother-liquor has become so much increased by washing as often to require concentration before being treated for substances yet in solution. Evaporation may be conducted in a wide bowl or basin, either over a lamp or on the sand bath. Boiling should be avoided, and for this purpose the bowl may be most securely placed upon a copper bath (about five inches in diameter) shown in

Fig. 10.

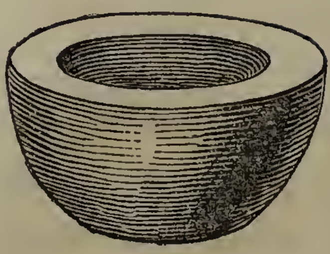
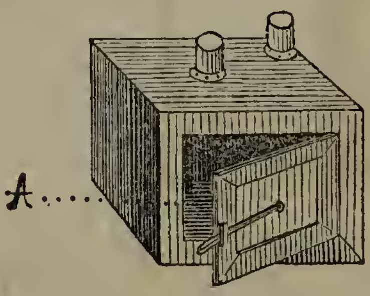


fig. 10, which is provided with rings to receive bowls of different sizes, and is supported by a tripod; being partly filled with water, it is heated by a small alcohol lamp. To prevent dust from falling into the bowl, it may be covered with filter-paper, (supported by a glass rod, or closely bent over the edge of the bowl). When the bowl is nearly full, the substance may often be prevented from creeping over the margin by slightly touching the latter with tallow. In evaporating to dryness, the process is facilitated by stirring. In quantitative analysis, a large bowl may be necessary for concentrating the solution, and a platinum basin for evaporating to dryness.

DRYING.

In quantitative analysis it is necessary thoroughly to dry a substance before weighing the portion designed for analysis. The pulverized substance is spread upon a weighed watch-glass, and placed in chamber *A*, of the accompanying water bath, fig. 11. This bath has double walls surrounding chamber *A*, and the space between these walls is filled with water, kept boiling by a lamp or uniform fire. After from two to four hours' drying, a second weighed watch-glass (also hot) is covered over the first; these are then removed from the water bath, left to partially cool, and then weighed. The substance is then returned to the bath, heated as before, and again weighed, repeating the operation so long as the weight diminishes.

Fig. 11.

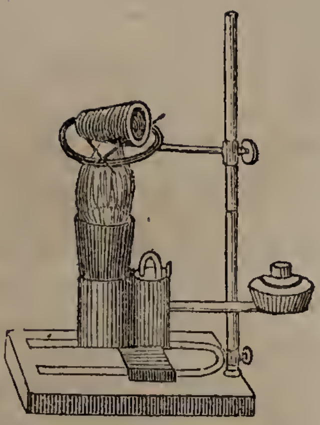


Filters containing precipitates to be dried, should be folded at the edge so as to enwrap the precipitate, and then exposed in a funnel to a gentle heat until nearly dry, then placed in bath fig. 11, until they cease to lose weight.

INCINERATION OF FILTERS.

When drying is insufficient, and the substance requires ignition before being weighed, it is also necessary to burn the filter to ash in order to subtract the weight of the latter from the total weight. As this incin-

Fig. 12.



eration is a delicate process, it must be conducted in a place free from currents of air. The precipitate is first carefully emptied from the filter into a platinum or porcelain crucible (over a sheet of thin glazed paper from which a fallen particle may be recovered), the folds of the filter being gently rubbed together to remove the adhering precipitate; the filter is then cut into small pieces and exposed, upon the cover of the crucible, to the flame of Berzelius' lamp, fig. 12. To complete the incineration, the carbonaceous particles remaining may be pressed upon the hot platinum by a small glass rod. This ash is added to the precipitate in the crucible, covered, ignited, and then cooled and weighed. Combustion and ignition are often facilitated by placing the crucible obliquely over the flame, as in fig. 12, so that there may be a current of air down into the crucible.

WEIGHING.

Weighing, though apparently a simple operation, is often the source of very vexatious errors, therefore great care must be taken that the working of the balance be not in any way disturbed, and that it, and the weights be not worn or corroded, thus preventing accurate results. A fine balance should always be kept in a room apart from chemical reagents. To avoid currents of air, the weighing is completed (in all the best balances) under a closed glass case. On the same account a substance which has been ignited should be allowed to cool before weighing, except where there is danger of its absorbing moisture from the air. The tare of filters and of their ashes is most readily controlled by cutting a large number of filters of a requisite size from paper of uniform thickness, drying five of these, at boiling heat, until they cease to lose weight, and then incinerating them. One fifth of the weight of the dried filters or of the ash will be the tare to be subtracted in weighing with this set of filters.

As French weights are now employed by practical chemists of every country, a comparative table is subjoined.

WEIGHTS AND MEASURES.

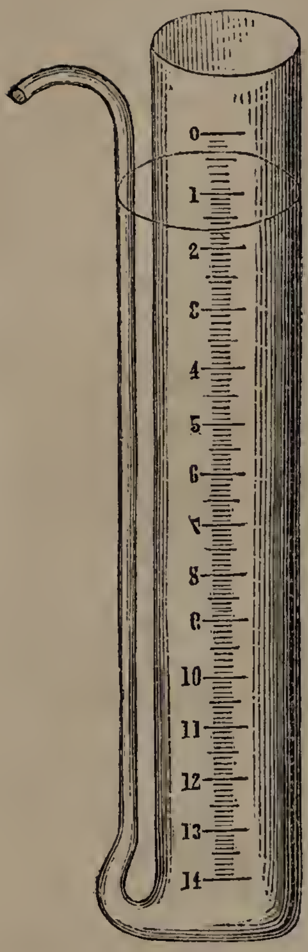
	French.		*English.*		
One	Milligramme	=	.0154	grains	Troy.
"	Centigramme	=	.1543	"	"
"	Decigramme	=	1.5434	"	"
"	Gramme	=	15.4336	"	"
"	Decagramme	=	154.336	"	"
"	Hectogramme	=	1543.36	"	"
"	Kilogramme	=	15433.6	"	"
		=	2.679	lbs.	Troy,
		=	2.205	"	Avoirdupois.

	French.		*English.*	
One	Millimètre	=	.0394	inches.
"	Centimètre	=	.394	"
"	Decimètre	=	3.937	"
"	Mètre	=	39.37	"
"	Decamètre	=	393.71	"
"	Hectomètre	=	3937.1	"
"	Kilomètre	=	39371.	"
"	Myriamètre	=	393710.	"

NOTE. — The scale of the centigrade thermometer, used in this work, may be readily made to correspond with that of Fahrenheit by multiplying by $\frac{9}{5}$ and adding 32 to the product.

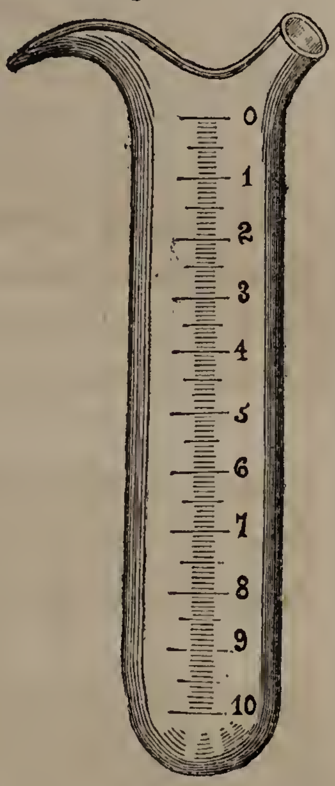
VOLUMETRIC ANALYSIS.

Fig. 13.



Volumetric analysis (see pp. 224, 231) is completed with such rapidity as to make the method very convenient where many similar analyses are to be performed. (Alkalimetry, acidimetry, and chlorimetry in commerce; testing urine in medical practice, etc.) It requires a burette, figs. 13 and 14, (14 is the better form), a cylinder (best with a foot) and a pipette, all graduated in ½ cubic centimetres, a beaker-glass, stirring rod, litmus-paper or other tests, together with a test solution of known strength. The burette is filled to zero with the test solution. (See page 224.)

Fig. 14.

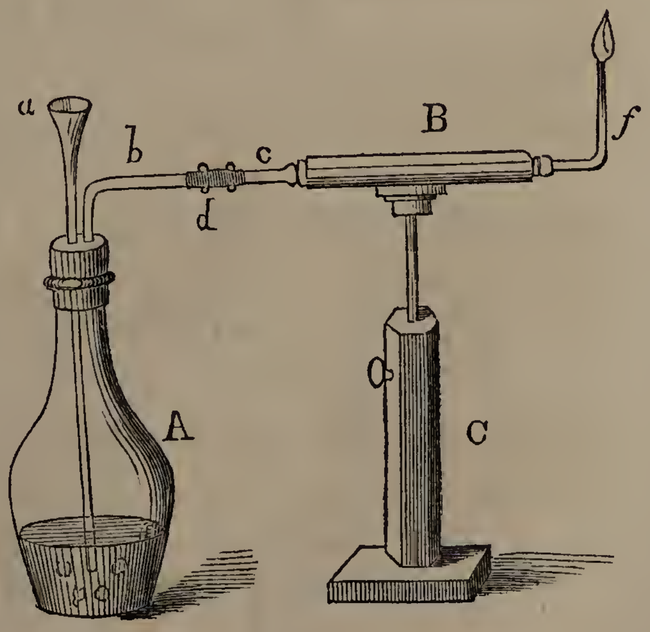


MARSH'S APPARATUS.

In Marsh's apparatus, fig. 15, *A* is the gas evolving bottle, provided with funnel tube *a*, and escape tube *b*. *B* is a chloride of calcium tube supported by stand *C*. Tube *b* is connected to *c* by india-rubber joint *d*. The gas issues at point of tube *f*, where it may be inflamed. (See pp. 80–90.)

A simple apparatus, consisting of a test tube provided with a cork and pointed tube may serve in many experiments.

Fig. 15.



APPARATUS.

As it may be useful for the student to anticipate his own wants in regard to apparatus and reagents, his time will be somewhat economized by the subjoined imperfect enumeration of articles required in a private laboratory, especially in processes of inorganic analyses.

Balance, turning with from one to one tenth millegramme.
Basin, of platinum, 2 to 3 inches diameter, 20 to 40 grammes weight.
Bath, copper, fig. 11, 5 to 8 inches wide.
“ “ “ 10, 4 to 8 inches diameter.
Beaker-glasses, form fig. 8½, 3 nests of 8, from ½ gill to 1 pint.
Blow-pipe, brass, fig. 4, with platinum tip.
Bottles, for reagents, 3 to 6 doz. 8 oz., ½ doz. 2 oz.
“ 1 doz. 4 oz. with large mouth.
“ 1 doz. assorted, for gas evolving, fig. 2, etc.
“ Woulff's, 4 to 8 oz. are convenient.
Bowls, porcelain, ½ doz., 5 inches in diameter.
“ “ ½ doz. assorted, 3 to 9 inches diameter, (see capsules).
Burette, fig. 14.
Capsules, porcelain, 1 doz. 1 inch diameter.
“ “ ½ doz. 2 “ “
Condenser, Liebig's, fig. 1 A., 2 to 3 feet long.
Corks, 4 doz. best velvet, ½ inch diameter.
“ 4 doz. free from holes, 1 to 2 inches diameter.
“ 4 doz. assorted.
Cork-borer, brass, with 12 sizes.
Crucible, platinum, with concave cover.
“ Hessian, 2 nests, 3 to 8 inches high.
“ porcelain, ½ doz. ½ inch diameter.
“ “ 1 “ “
“ “ 1½ “ “

Cylinder-glass, graduated in $\frac{1}{2}$ cub. cent.
Files, rat tail, small quill size and larger, (for fitting corks to tubes).
" very small triangular, (for cutting glass tubes).
Filter-stand, fig. 8$\frac{1}{2}$.
Flasks, thin glass, with flattened bottoms, fig. 7, $\frac{1}{2}$ doz. 2 oz., $\frac{1}{2}$ doz. 6 oz., $\frac{1}{4}$ doz. 1 quart, $\frac{1}{4}$ doz. 3 quarts.
Forceps, steel, very small, and one large; also with platinum points.
Funnels, glass, 1 doz. assorted, 1 inch to 6 in diameter.
Funnel-tubes, fig. 2 *a*, $\frac{1}{4}$ doz.
Furnace, portable, fig. 1, *O.*
India-rubber, sheet, 1 square foot.
Lamp, brass, Berzelius', fig. 12, and 2 doz. wicks.
" glass, small alcohol, fig. 4.
Mortar, steel, fig. 5,
" agate, 2 to 3 inches diameter.
" Wedgwood's ware, 4 to 5 inches diameter, and not deep.
Paper (filter paper), quires 3.
Pipette, glass, graduated in $\frac{1}{2}$ cub. cent.
" bulb-formed.
Platinum foil, thin, 2 pieces, or more, 3 inches by $\frac{3}{4}$.
" wire, very fine, 1 foot or more.
" see basin and crucible.
Rack, for test tubes.
Receiver, spherical, with 2 tubes, 6 inches in diameter.
Retorts, $\frac{1}{2}$ doz. assorted, 2 oz. to 12, (little used, as flasks are more easily cleaned).
Retort-holder, fig. 1, *C.*
Rods, glass, quill size assorted, 1 pound or more.
Sand-bath, any iron pan; also a small hemispherical basin from wrought iron.
Spatula, porcelain, (platinum is better).
Suction tube, fig. 8.
Tripod, sheet-iron, six inches high.
Tubes, chloride of calcium tubes (Liebig's), $\frac{1}{4}$ doz.
" quill tubes various sizes, 2 to 8 pounds.
" $\frac{1}{2}$ inch to 1 diameter, and 3 feet long, $\frac{1}{4}$ doz.
Triangles, iron wire, $\frac{1}{2}$ doz. small.
Watch-glasses, in pairs, 1 doz.
Weights, set from 50 grammes to $\frac{1}{4}$ millegr.; (small weights should be platinum) better from 100 grammes downward.

REAGENTS.

REAGENTS must be procured from some reliable source until the student shall have learned to prepare them, or at least to test them for himself. Of the principal reagents, the following is a limited supply for a beginner.

Acid, acetic,	lbs.	5
“ chlorhydric,	“	5
“ nitric,	“	3
“ oxalic,	“	½
“ phosphoric,	“	⅛
“ sulphuric,	“	3
“ tartaric,	“	½
Alcohol,	galls.	2–5
Ammonia, aqueous,	lbs.	5
“ carbonate,	“	2
“ oxalate,	“	½
Ammonia-soda, phosphate,	“	¼
Ammonium, chloride,	“	1
Barium, chloride,	“	½
Baryta, hydrate,	oz.	1
“ nitrate,	“	2
Borax, fused,	lbs.	½
Calcium, chloride, fused,	“	¼
“ fluoride,	“	1
Cobalt, nitrate, (solution)	oz.	¼
Copper, turnings,	lbs.	½
Ether,	“	1–5
Iron, filings,	“	3–5
“ terchloride,	“	⅛

Iodine,	oz.	$\frac{1}{4}$
Lead, neutral acetate,	lbs.	$\frac{1}{4}$
Lime, caustic,	“	1
“ carbonate,	“	1
Litmus-paper,	sheets, doz.	1
Magnesia, carbonate,	lbs.	1
Manganese, black oxide,	“	5
Mercury, chloride (coros. sub.),	oz.	2
Platinum, bichloride (solution),	“	1–2
Potassa, acetate,	lbs.	$\frac{1}{4}$
“ carbonate,	“	$\frac{1}{2}$
“ caustic,	“	$\frac{1}{4}$
“ nitrate,	“	$\frac{1}{2}$
Potassium, cyanide,	“	$\frac{1}{4}$
“ ferrocyanide,	“	$\frac{1}{4}$
“ ferricyanide,	“	$\frac{1}{4}$
× Silver, nitrate (crystalline),	oz.	$\frac{1}{2}$
× Soda, carbonate,	lbs.	3
× “ caustic,	oz.	2
“ phosphate,	“	4
Sulphur,	lbs.	5
Tin, protochloride,	oz.	2
Turmeric-paper,	sheets, doz.	1
Zinc, granular,	lbs.	$\frac{1}{2}$

× CaOCl,

CORRIGENDA.

Page 28, line 8 from top, for *which* read *since they;* p. 28, l. 11 from top, for *also* read *as;* p. 32, l. 16 from top, for *nickel* read *nickel-speiss;* p. 38, l. 1, for *in* read *of;* p. 39, l. 18 from top, for *peroxide* read *binoxide;* p. 41, l. 20 from top, for *peroxide* read *binoxide;* p. 56, l. 9 from bottom, for *hypochlorite* read *hyposulphite;* p. 59, l. 9 from bottom, for *protochlorite* read *protochloride;* p. 75, l. 11 from bottom, for *peroxide* read *binoxide;* p. 90, l. 2 from bottom, for *close* read *closed;* p. 111, l. 6 from top, for *by* read *through;* p. 121, l. 15 from top, for *then* read *there;* p. 123, l. 10 from top, for $(Fe\,O + F_2\,O_2)$ read $(Fe\,O + Fe_2\,O_3)$; p. 125, l. 4 from bottom, for *also* read *even;* p. 127, l. 9 from top, for *phosphorus* read *phosphorous;* p. 134, l. 2 from top, for $Cr\,O\,Cl$ read $Cr\,O_2\,Cl$; p. 148, l. 17 from top, for *mixed* read *is mixed;* p. 161, l. 10 from bottom, for *compounds* read *compound;* p. 168, l. 4 from top, for Co read C O; p. 192, l. 6 from bottom, for 80.72 read 80:72; p. 208, l. 14 from top, for *abfiltered* read *filtered off;* p. 210, l. 3 from top, for *in* read *of;* p. 227, line 1, for 5 × 49 read 5 × 4,9; p. 230, l. 12 from top, for 4.36 read 43.6; p. 235, l. 11 from bottom, for P I read p I; p. 239, l. 10 from top, for *diluted* read *diluted at* 15° C.

Table I. column 5, for *oxide of tin* read *binoxide of tin;* col. 6, for *silenium* read *selenium.* Table II., cols. 1, 2, 3, and 4, for *oxide of tin* read *binoxide of tin.* Table III., col. 1 f., for *oxide of tin* read *binoxide of tin.* Table VII., l. 2 from top, for *Zinc* read *Lime.* Table VIII., col. 3, l. 6 from top, for *potassa* read *soda;* col. 1, l. 7 from bottom, for *potassa* read *lime.* Table IX., l. 7 from top, for *vapor or gas are colorless* read *colorless vapor or gas;* col. 3, l. 1, for *colorless* read *inodorous;* col. 4, l. 7 from top, before *evolves* insert *with dilute chlorhydric acid;* col. 5, l. 16 from top, omit *ferric oxide.* Table XI., col. 3, l. 7 from top, for H S read S H.

OUTLINES

OF

QUALITATIVE ANALYSIS.

PART FIRST.

COMPORTMENT OF THE METALLIC OXIDES AND THEIR SALTS.

GROUP I.

THE ALKALIES.

Potassa, Soda (*Lithia*), *and Ammonia.*[*]— The metals of the alkalies (*Potassium* K, *Sodium* Na, and *Lithium* Li) are lighter than water, which they decompose at ordinary temperatures, disengaging hydrogen gas and forming oxides (the fixed alkalies, KO, NaO, LiO), which are soluble in water, giving it a caustic taste and the property of coloring reddened litmus paper blue, and turmeric paper brown. The compounds of these metals with

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[*] Substances of rare occurrence are inclosed in brackets. Ammonia is included in this group on account of its relation to the fixed alkalies.

chlorine, bromine, iodine, fluorine, cyanogen, and sulphur are likewise soluble in water, as also the compounds of the alkalies with most of the inorganic and organic acids.

1. Potassa. KO.

$KO\ CO_2$

Potassa is very abundant in the mineral kingdom, being found in Felspar, Mica, Clay, Soil, the ashes of plants, and in many mineral springs.

$KCl + PtCl_2 = KCl, PtCl$

Bichloride of platinum, in moderately dilute solutions of the salts of potassa, gives an orange-yellow, crystalline precipitate — the double chloride of platinum and potassium ($KCl, PtCl_2$); in seeking for small quantities of potassa, the solution mixed with the bichloride of platinum and a little chlorhydric acid is evaporated quite to dryness and then treated with alcohol, when the double salt will remain insoluble.

$KCl + (HO)_2\ \bar{T} = KO\ \bar{T}, HO + HCl$

Tartaric acid, on being added to potassa salts until there is a decided acid reaction, gives a crystalline precipitate, which appears, either immediately or after a short time, according to the concentration of the potassa. Violent agitation hastens the formation of the precipitate (bitartrate of potassa $C_8H_4O_{10}, KO, HO$). It requires 180 parts of cold water to dissolve it, although it is readily soluble in the mineral acids and in alkaline liquids.

Pure salts of potassa, free from soda, give a *violet* color to the outer flame of the blowpipe, which however is not equally manifest with all. If alcohol be mixed with a moderately dilute solution of a salt of potassa heated and ignited, it will burn with a violet flame.

2. SODA. NaO.

Soda, like potassa, is found abundantly in the mineral kingdom. It can be recognized (even in the presence of the two other fixed alkalies) by the intense yellow color its salts impart to the flame of alcohol, or to the outer flame of the blowpipe..

Since soda forms very few insoluble compounds with acids, we have but few reliable reagents by which it can be separated in an insoluble form from its solutions. N

Meta-antimoniate of potassa, 2 KO, SbO_5, when carefully prepared and in fresh solution, gives, in a moderately dilute solution of a *neutral* or only slightly alkaline salt of soda, a white precipitate of the meta-antimoniate of soda (NaO, SbO_5). The alkaline earths or oxides of the heavy metals must not be present when the reagent is employed. $NaCl + HO + 2KO, SbO_5 = NaO\ SbO_5 + HCl + 2KO$

3. [LITHIA.] LiO.

Lithia is found in small quantities in Petalite, Spodumene, Amblygonite, Lepidolite, Triphylline, and also in mineral springs.

The salts of lithia are all soluble in water; but as the carbonate and phosphate are with difficulty soluble, the *carbonate of soda* or the *phosphate of soda* will give precipitates in concentrated solutions of the salts of lithia, especially when they are heated and somewhat evaporated.

It is not precipitated by the bichloride of platinum and tartaric acid. The chloride of lithium is deliquescent and soluble in a mixture of anhydrous ether and alcohol, which latter fact distinguishes it from the chloride of sodium.

The salts of lithia impart a carmine color to the blowpipe flame and to that of alcohol, which is not prevented by the presence of potassa, though concealed by the presence of the salts of soda.

When heated along with carbonate of soda on platinum foil, they produce a dark yellow tarnish on the platinum, the warm melted mass is transparent.

For the exhibition of the lithia in Triphylline ($3 (LiO, MnO, FeO), PO_5$), the solution of the mineral in nitrochlorhydric acid is evaporated to dryness, treated with hot water, and digested with some hydrate of lime. The filtered solution is freed from the lime by means of ammonia and carbonate of ammonia, and then evaporated, when the chloride of lithium will be obtained after exposure to violent heat.

For the detection of *potassa, soda,* (and also lithia) in silicates, which are not decomposed by chlorhydric acid, they are mixed, in a finely pulverized condition, with three or four times their weight of hydrate of baryta freed from water, carbonate of baryta or caustic lime, and exposed to a red heat for some time in a platinum crucible. The mass when cold is pulverized and lixiviated with hot water. The solution, thus obtained, is saturated with chlorhydric acid, and is evaporated with the addition of ammonia and carbonate of ammonia. This is again filtered, evaporated to dryness, and the residue ignited. It contains the alkalies as chlorides of their metals. Or the mineral is completely decomposed by fluohydric acid, evaporated along with concentrated sulphuric acid to dryness (for the separation of the fluoride of silicium from the silico-fluorides of the metals), treated with hot water, ammonia, and carbonate of ammonia, which precipitate alumina, the sesquioxide of iron, etc. This is again filtered, evaporated, and ignited, when the alkalies are obtained as sulphates. If magnesia is present, it must be treated as described on page 11, before the alkalies are separated. Limestones, containing alkalies, are intensely ignited, and then the solution which they give with hot water, along with some carbonate of ammonia, is evaporated and treated as above.

Potassa is recognized in a mixture of the salts of the fixed alkalies, by its being precipitated with the bichloride of platinum or tartaric acid; *Soda*, by the yellow color it gives to the flame of alcohol or to that of the blowpipe; *Lithia*, on account of being precipitated (in concentrated solution) by carbonate and phosphate of soda, and the carmine color it gives to flame.

KO
NaO
LiO

4. AMMONIA. NH_3.

NH_4Cl

This is very abundant in the atmosphere, in black mould or soil, in the juices of plants, etc.

If a salt of ammonia be heated along with a caustic alkali (best with hydrate of lime), the ammonia is set free in a gaseous form, and can easily be recognized by its characteristic odor, and by the white clouds of chloride of ammonium, which are formed when a rod, moistened with non-fuming chlorhydric acid, is brought near it.

Free ammonia may be recognized in small quantities, if the fluid to be tested be mixed with an excess of hydrate of lime and placed in a watch glass along with some white filter paper that has been moistened with a very small quantity of the solution of sulphate of copper or manganese, the whole being covered with a glass plate. In the one case there would be an azure blue, and in the other a brown spot produced.

A solution of *molybdate of soda* in chlorhydric acid, containing a little *phosphoric acid* (30 pts. of $Mo\,O_3$ to 1 pt. of $P\,O_5$), gives in liquids containing ammonia, a yellow precipitate, which in a very dilute solution, only appears after long standing; it is soluble in alkalies and in the non-volatile organic acids.

Neutral *subnitrate of Mercury* gives a brown color, in solutions which contain only a very small quantity of *free* ammonia. Ammonia salts, made weakly alkaline, precipitate corrosive sublimate white.

The salts of ammonia comport themselves with *bichloride of platinum* and *tartaric acid,* like the salts of potassa. The precipitate, in the case of the bichloride of platinum ($N\,H_4\,Cl$, $Pt\,Cl_2$), is insoluble in alcohol and ether, disengages ammonia when mixed with potassa, and leaves behind pure platinum on exposure to heat, from which no chlorine compound can be extracted by water; the precipitate by tartaric acid ($C_8\,H_4\,O_{10}$, $N\,H_4\,O$, $H\,O$), on being ignited gives a carbonaceous residue with no alkaline reaction.

All the salts of ammonia are volatile at a red heat, some by decomposition, as the sulphate or nitrate, and others without being decomposed as the chloride.

There are several volatile organic bases (Methylamin $C_2\,H_5\,N$, Aethylamin $C_4\,H_7\,N$, etc.) which resemble ammonia very closely in all their properties.

GROUP II.

THE ALKALINE EARTHS.

Baryta, Strontia, Lime, and Magnesia.—The metals of the alkaline earths (*Barium* Ba, *Strontium* Sr, *Calcium* Ca, *Magnesium* Mg), like those of the alkalies, decompose water without the coöperation of an acid. Their oxides, the alkaline earths (BaO, SrO, CaO), are soluble in water, though with more difficulty than the alkalies. Their solutions have alkaline reactions. Magnesia (MgO) is insoluble in water, though with difficulty soluble when a hydrate. All the alkaline earths form compounds with carbonic and phosphoric acid which are insoluble in water; hence they are precipitated from their neutral solutions by the soluble and neutral salts of these acids. Their sulphates are either insoluble in water and acids (baryta and strontia), or with difficulty soluble (lime), or very soluble (magnesia). As the metals of this group form compounds with sulphur which are soluble in water, and as their oxides, in combination with acids, are not decomposed by sulphydric acid into water and the sulphides, the solutions of the alkaline earths will not give precipitates with sulphydric acid, and those of their salts only afford precipitates with the sulphide of ammonium, when an acid (phosphoric for example) is present, with which the alkaline earth forms a salt insoluble in water; the precipitate is not a sulphide but a salt (phosphate) of the alkaline earth.

1. Baryta. BaO.

Ba Cl

This is found as heavy spar (BaO, SO_3) and Witherite (BaO, CO_2).

The salts of baryta, which are soluble in water, are not precipitated by ammonia; the *carbonates* of the *fixed alkalies* and *carbonate of ammonia* (the latter requiring the addition of free ammonia and gentle warmth) precipitate baryta completely as the carbonate (BaO, CO_2).

Free sulphuric acid, or any soluble *sulphate* will precipitate this base completely, even from those salts which are only soluble in acids, in the form of sulphate of baryta (BaO, SO_3), insoluble in all dilute acids or alkaline solutions.

The salts of baryta are also precipitated by *sulphate* and *chromate of strontia.* (A reaction distinguishing it from strontia and lime.)

Silico-fluo-hydric acid produces, even in acid solutions of baryta, an almost transparent precipitate of the silico-fluoride of barium ($3\,BaFl, 2\,SiFl_3$) which can only be recognized after its deposition.

Phosphate of soda throws down, in neutral salts of baryta, the phosphate of baryta ($2\,BaO, HO, PO_5$) which is very soluble in chlorhydric, nitric, and acetic acid.

Most of the salts of baryta communicate a greenish-yellow color to the flame of alcohol.

2. Strontia. SrO.

Found as Celestine (SrO, SO_3) and Strontianite (SrO, CO_2).

The salts of strontia comport themselves with reagents like those of baryta. The sulphate of strontia is not so insoluble in water and acids as the sulphate of baryta, on which account in a moderately dilute solution of strontia, the precipitate of its sulphate does not immediately appear on the addition of sulphate of lime or any other soluble sulphate, though it will appear sooner or later.

Silico-fluo-hydric acid gives no precipitate with strontia.

The salts of strontia, which are soluble in alcohol (as the nitrate of strontia, and also the chloride of strontium) give a crimson color to its flame.

Strontia is recognized, when mixed with baryta, by first bringing both to the condition of chlorides, (which is done by dissolving the carbonates in chlorhydric acid, and evaporating to dryness,) and then digesting with strong alcohol. After filtration, the alcohol is ignited and stirred around.* A mixture of the sulphates of baryta and strontia should be boiled with a concentrated solution of carbonate of soda, filtered when *hot*, and the carbonates thus formed, after being washed, dissolved in chlorhydric or nitric acid, and treated as above. The baryta can be separated in the solution by silico-fluo-hydric acid, and the strontia be detected in the filtrate by sulphuric acid.

3. LIME. CaO.

Ca O CO.

This is very extensively distributed in the three kingdoms of nature, especially as sulphate, carbonate, phosphate, and silicate; and also as chloride of calcium. The salts of lime behave towards reagents very much like those of baryta and strontia.

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* This will give the red flame indicative of strontia, with a yellowish tinge. It may also be remarked that the chloride of barium is almost insoluble in alcohol. L. H. S.

Very dilute solutions of lime will not give a precipitate along with *sulphuric acid* or *the sulphates*, whereby it is distinguished from baryta and strontia. Concentrated solutions give a white precipitate of the sulphate of lime ($CaO, SO_3, 2HO$), which requires 500 parts of water to effect its solution, though it is more soluble in acids, and quite insoluble in alcohol, on which account the addition of alcohol to a solution of lime will always insure its precipitation by sulphuric acid.

Oxalic acid or the *soluble oxalates* will precipitate lime, even in very dilute solutions, as an oxalate ($CaO, C_2O_3, 2aq$). This is quite insoluble in water, acetic acid, and oxalic acid, though readily soluble in the mineral acids. Free ammonia hastens its formation.

Some of the salts of lime (the chloride of calcium and the nitrate of lime) are soluble in alcohol, and impart a *yellowish-red* color to its flame.

For the detection of lime in the presence of baryta and strontia, the latter are thrown down *entirely* by the use of dilute sulphuric acid or the sulphate of potassa, the solution is heated to ebullition and filtered. The filtrate is then neutralized with ammonia, and precipitated by an oxalate. The lime will be shown, if small quantities are present, often only after some time, and will be proved by the insolubility of the precipitate in acetic acid.

4. MAGNESIA. MgO.

This is an almost constant companion of lime. It occupies in its reactions, a midway between the alkaline earths and the earths. Its salts are precipitated by the *carbonates of the fixed alkalies*, making a gelatinous precipitate — the basic carbonate of magnesia ($3MgO, 3CO_2 + MgO, HO$); this precipitation is complete only at the boiling point. *Caustic potassa* and *soda,* as also *baryta* and *lime water,* throw down the hydrate (MgO, HO). All these precipitates are soluble on the addition of a sufficient quantity of a salt of ammonia, or they are not produced if this is already present.

Ammonia, in neutral salts of magnesia, throws down one half as the hydrate, while the other half remains in solution with the salt of ammonia that has been formed as a double salt, which is not decomposed by additional ammonia.[*] Chloride of ammonium (or any other ammoniacal salt) dissolves the precipitated hydrate of magnesia, with the evolution of some ammonia, and the formation of a double salt.[†] If the solution of the magnesian salt contain a sufficient quantity of free acid, then ammonia will produce no precipitate, since all the magnesia passes over into the double salt just mentioned.

The salts of magnesia comport themselves with the *carbonate of ammonia,* as with ammonia, and in the same way with the fixed alkalies and their carbonates, if ammonia be present. They are not precipitated in the cold by the bicarbonate of ammonia, and only partially and slowly by the carbonate, though the precipitate is produced more quickly on ebullition.

Phosphate of soda ($2\,NaO, HO, PO_5$) — in the absence of ammonia — gives a precipitate only in concentrated solutions of magnesian salts ($2\,MgO, HO, PO_5 + 7\,Aq$); but when free ammonia is present, the whole of the magnesia is precipitated as a crystalline phosphate of ammonia-magnesia ($2\,MgO, NH_4O, PO_5 + 12\,aq$), which is slightly soluble in pure water, though insoluble

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[*] $2\,(MgO, SO_3) + NH_4O, HO = MgO, HO, + (MgO, SO_3 + NH_4O, SO_3)$.

[†] $MgO, HO + 2\,NH_4Cl = (MgCl, NH_4Cl) + NH_4O, HO$.

in dilute ammonia, or any of its salts. In looking for small quantities of magnesia, the fluids should be exposed to gentle warmth. By rubbing the sides of the vessel with a glass rod, the separation of the compound will be aided. This precipitate is soluble in all the acids, not even excepting acetic acid.

Oxalic acid produces no precipitate with the salts of magnesia if they are mixed with those of ammonia.

When magnesian salts are heated on charcoal by means of the blowpipe flame, the glowing salt being moistened with a solution of nitrate of cobalt, and again still more powerfully heated for some time, it assumes a pale-red color. This action is not perceptible if other metallic oxides are present.

Magnesia can be separated from baryta, strontia, and lime, by carbonate of ammonia, in the presence of a salt of ammonia and free ammonia. It remains completely in solution, while the baryta, strontia, and lime (on the application of gentle warmth) are precipitated. If the filtrate gives, whether sooner or later, a crystalline precipitate on the addition of phosphate of soda, then magnesia is present.

For the detection of potassa, soda, and lithia in combination with magnesia and the other alkaline earths, the following methods are available: —

1. We precipitate the alkaline earths as phosphates, by means of *phosphate of ammonia*, free ammonia and a few drops of chloride of ammonium being added to the heated solution; then the excess of phosphoric acid can be removed by adding acetate of lead, and the excess of the oxide of lead by means of ammonia and carbonate of ammonia. The filtrate will contain the fixed alkalies along with ammoniacal salts, and the former can be freed from the latter by evaporation and ignition.

2. The salts of ammonia may be removed by evaporating the solution to dryness, and igniting the residue. The latter can then be treated with water, and the solution thus formed with baryta water (the sulphide of barium will answer as well), so long as a precipitate occurs, after which it is warmed and filtered. The excess of baryta being removed from the filtrate by carbonate of ammonia or by sulphuric acid, it can then be evaporated and ignited. The residue contains the alkalies. If the solution contains no salts of ammonia, the first evaporation and ignition can be omitted, since in this case the magnesia will be completely precipitated by the baryta water.

The salts of the alkaline earths, which are soluble in water, are *not* precipitated by ammonia or sulphide of ammonium (except magnesia, which is precipitated by only, not ammonia when a sufficient quantity of any salt of ammonia is present); it is different, however, with those which are insoluble in water, but soluble in acids without decomposition (so far as their acids remain in the solution), also with those in combination with phosphoric, arsenic, fluo-hydric, and oxalic acid, and also many non-volatile organic acids. This applies especially to the compounds of lime with nearly all the above acids, but in the case of magnesia, only to the common phosphate and arseniate. If these salts are dissolved in an acid, they are thrown down on being neutralized with ammonia or (what is here the same thing, with the exception of the arseniate) with the sulphide of ammonium. They exhibit the same comportment as the earths towards the common reagents; they are insoluble in potassa.

If the acid in combination with the alkaline earth be oxalic or any other organic acid, then the precipitate, after ignition, will effervesce on the addition of acids; in

The simple MgO.HO is quite insoluble and f no NH_4 Salt be present ½ of it falls see P 11.

this case the base, after it is dissolved in chlorhydric acid, cannot be precipitated by the addition of ammonia, and may be ascertained in the usual way. If the acid in combination with the alkaline earth is phosphoric (or arsenic) acid, then the precipitate is not decomposed by ignition, though the base can be detected, if we add cautiously to the solution of the salt in chlorhydric acid (there being not too much free acid present) acetate of soda and the sesquichloride of iron by drops, until the liquid becomes reddish; the liquid being heated to ebullition and filtered, the colorless filtrate will contain the alkaline earths as chlorides which can then be detected in the usual way; the precipitate contains all the phosphoric (or arsenic) acid as a basic salt of sesquioxide of iron. Or the solution of the precipitate in chlorhydric acid, mixed with acetate of soda, can be tested with oxalate of ammonia (for lime), or with sulphate of lime (for baryta and strontia), and finally the magnesia may be detected (after the separation of the baryta, strontia, or lime) by super-saturation with ammonia.

GROUP III.

THE EARTHS AND THE ALLIED METALLIC OXIDES.

Alumina (*Glucina, Zirconia, Thoria, Yttria, oxides of Erbium, Terbium, Cerium, Lanthanum,* and *Didymium; the oxides of Titanium, Tantalum, Niobium, Pelopium* and *Vanadium*) and *Chromium.*

The earths are mostly white, yellowish or brownish, infusible, pulverulent substances, becoming generally very luminous when exposed to a red heat, without alkaline reaction, quite insoluble in water, and with difficulty soluble in acids even at a red heat. They can be reduced either by hydrogen or carbon. They are separated from their salts by ammonia, sulphide of ammonium, and the fixed alkalies, in the form of gelatinous precipitates. Their acid and neutral solutions are not precipitated by sulphydric acid. The fact that they afford precipitates with ammonia and sulphide of ammonium, even in the presence of ammoniacal salts, distinguishes them essentially from the alkaline earths.

1. ALUMINA. Al_2O_3.

Very abundant in nature. It forms colorless salts with acids, some insoluble in water, and some soluble, having acid reactions, and which give up their acids on ignition, if they are volatile. Those compounds of alumina, which are insoluble in water, are mostly soluble in chlorhydric acid; and those natural compounds which are not decomposable by chlorhydric acid (aluminates), will be decomposed by being heated along with concentrated sulphuric acid (clay), bisulphate of potassa, or with the carbonate of potassa-soda, and the alumina is then made soluble in acids.

Caustic potassa and *soda* throw down, in solutions of alumina in acids, basic salts of alumina, as gelatinous precipitates, which are redissolved in an excess of the alkali. From such an alkaline solution, the alumina may be again completely precipitated by the addition of a sufficient quantity of chloride of ammonium (or better, by neutralizing with chlorhydric acid and adding excess of ammonia); sulphydric acid will not produce a precipitate in such a solution.

Ammonia, carbonate of ammonia, and *sulphide of ammonium* throw down the base, from the salts of alumina, as a gelatinous hydrate (Al_2O_3, $3HO$) which is somewhat soluble in large excess of ammonia, though not soluble in the two last-named reagents. The carbonates of the fixed alkalies also precipitate the hydrate of alumina, which is soluble in large excess of concentrated solutions of these reagents.

Phosphate of soda precipitates, in solutions of the salts of alumina, a gelatinous phosphate (Al_2O_3, PO_5, $6HO$), which is soluble in potassa-lye and in acetic acid. If an alkaline silicate be added to a solution of alumina, or of the phosphate of alumina in caustic alkali, there will be produced a precipitate of the silicate of alumina, and the phosphoric acid will remain in the solution.

Chloride of barium, or *baryta-water,* removes from a solution of the phosphate of alumina, in caustic alkali, all the phosphoric acid as phosphate of baryta, the alumina remaining entirely in solution, provided it is heated along with excess of the alkali.

On the addition of sulphate of potassa to hot, concentrated solutions of the salts of alumina, a precipitate will be produced, on cooling, of octahedral crystals of alum ($KO, SO_3 + Al_2O_3, 3SO_3 + 24aq$).

If a salt of alumina be ignited before the blowpipe, moistened with the cobalt solution, and then more intensely ignited, the residue will assume a beautiful blue color.

2. [Glucina. G_2O_3.]

Glucina has a very close resemblance to Alumina in all its reactions; it differs however from the latter by its solubility in carbonated alkalies, by its salts affording no precipitate of glucina-alum along with the sulphate of potassa, and by the fact that its dilute solution in the caustic alkalies is decomposed by long boiling, the earth being precipitated.

Alkaline carbonates throw down, in solutions of its salts, the carbonate of glucina, which is only soluble in considerable excess of the precipitant. A concentrated solution of carbonate of ammonia dissolves the precipitate more readily than either the carbonate of soda or potassa; but by boiling, the earth is again precipitated in such a solution.

If glucina be ignited along with the solution of cobalt, it will furnish a gray mass. The natural compounds of glucina (the Beryl ($G_2O_3, 2SiO_3 + Al_2O_3, 2SiO_3$), Euclase, Phenakite) are perfectly decomposed by being fused along with four times their weight of carbonate of potassa-soda.

3. [Zirconia. Zr_2O_3.]

Zirconia, as a hydrate, is very soluble in acids, though after ignition it is only soluble in concentrated sulphuric acid. *Ammonia,* and *caustic potassa* or *soda* produce, in solutions of zirconia, a precipitate of the hydrate, which is insoluble in excess of the precipitant, but soluble in carbonate of ammonia.

Sulphate of potassa throws down the white double sulphate of zirconia and potassa, which is almost insoluble in water and in acids.

Natural compounds of Zirconia (Zircons Zr_2O_3, SiO_3) can be decomposed by long fusion along with carbonate of soda. When this is treated with water the silicate of soda will be dissolved out, and a crystalline powder composed of zirconia and soda is left behind, which after being washed in water is soluble in chlorhydric acid, and the earth is precipitated as a hydrate by the addition of ammonia.

4. [THORIA. ThO.]

This earth is only found in Pyrochlore, Thorite, and Monazite. Its comportment with reagents is similar to that of zirconia. Its double salt, with sulphate of potassa, is soluble in pure water, and insoluble in sulphate of potassa. Thorite ($3\,ThO, SiO_3 + 3\,HO$) is decomposed by concentrated chlorhydric acid.

5. [YTTRIA, ERBIA, TERBIA.]

These are found in some rare minerals, such as Gadolinite, Orthite, and Yttrotantalite. They are insoluble in potassa, soluble in carbonate of ammonia, and are so similar in their reactions that the mode of separating them is not yet known.

6. [OXIDES OF CERIUM, CeO; Ce_2O_3; of LANTHANUM, LaO, and of DIDYMIUM DiO.]

These oxides are found in Cerite ($2 (SiO_3 \, 3 RO) + 3 \, aq$), along with the oxide of iron, lime, and some little of the sulphide of molybdenum and of bismuth. This mineral is not decomposable by chlorhydric acid or aqua-regia, though the decomposition can be completely effected by ignition along with carbonate of soda.

If the finely pulverized mineral be heated along with concentrated sulphuric acid, a few drops of nitric acid being added, and then cold water be poured on it, the sulphates of the above oxides will be dissolved out, and the silicic acid be left behind. A hot saturated solution of *sulphate of potassa*, in a moderately dilute solution, precipitates the three oxides as double salts, which, after being washed with a saturated solution of sulphate of potassa, and dissolved in boiling water containing some chlorhydric acid, are precipitated when warm by excess of potassa. Cold and very dilute *nitric acid* extracts the oxide of Lanthanum as the nitrate from the brown mixture of these oxides (freed from sulphuric acid), which, after its precipitation by carbonate of ammonia and its ignition, is white.

By repeated treatment of the mixture of the oxides with strong potassa lye and chlorine gas, the cerium becomes the yellow insoluble protoxide, while all the lanthanum and didymium dissolve as proto-chlorides. All three oxides are insoluble in potassa and ammonia, soluble in carbonate of ammonia, and form, with oxalic acid, salts which are difficult of solution.

The following oxides of the metals are included with earths, on account of their comportment with ammonia or the sulphide of ammonium.

7. [Oxides of Titanium.]

Titanic acid, TiO_2; *Sesquioxide of Titanium,* Ti_2O_3.— Titanic acid is the most important compound of Titanium; it occurs in Rutile, Anastase, and Brookite, and in combination with lime in Titanite ($2\,CaO, SiO_3 + CaO, 3\,TiO_2$). Titaniferous iron is Fe_2O_3, Ti_2O_3 and FeO, Ti_2O_3. The copper-colored cubes formed in furnaces are $TiCy, 3\,Ti_3N$.

Ignited and native titanic acid are only dissolved by fluo-hydric acid, or with difficulty by concentrated sulphuric acid. The precipitated acid, however, when washed with *cold* water, is soluble in cold concentrated chlorhydric acid, from which solution, after sufficient dilution, it is again precipitated by boiling, provided there be not too much acid present. This precipitation is more easily and completely effected on the addition of sulphite of soda at the boiling point. Titanic acid is precipitated from its solutions by ammonia and sulphide of ammonium, and in a gelatinous form by the caustic or carbonated alkalies; the presence of alcohol prevents these precipitates.

Oxalic acid produces in solutions of titanic acid, which are not too acid, a white, and *ferrocyanide of potassium,* a reddish brown precipitate, which, in the latter case, is green if iron be present.

If *metallic zinc* (*tin* or *iron*) is placed in a solution of titanic acid in chlorhydric acid, it will reduce the titanic acid to the sesquioxide of titanium, which at first remaining in solution, gives it a blue or violet color, but by longer action of the zinc it is thrown down as a violet powder.

Pure titanic acid by continued exposure to the reduction flame of the blowpipe, imparts to the cooled beads of the phosphate of ammonia-soda and borax, a violet color. This action is more readily shown by the addition of tin; the color disappears in the oxidation flame. Titanic acid containing iron gives a blood red pearl in the inner flame. When fused on charcoal along with soda or cyanide of potassium, it does not form a metallic granule which distinguishes it from the oxide of tin.

When heated by itself, titanic acid becomes yellow.

If native titanic acid (Rutile) in a very finely pulverized condition be fused along with four times its weight of carbonated alkali, and treated with cold water, a crystalline acid titanate of the alkali will remain along with some sesquioxide of iron. This should be digested with concentrated chlorhydric acid, and the diluted solution boiled along with sulphite of soda, when the titanic acid will be precipitated; or we may precipitate with sulphide of ammonium and pour sulphurous acid over the precipitated mixture of the sulphide of iron and titanic acid, when the former will be dissolved out, and the latter left behind as a white powder. Or the fused mass may be treated with dilute fluo-hydric acid in a platinum capsule, and the fluo-titanide of potassium thus formed, which is hardly soluble, may be purified by crystallization from hot water, and the salt decomposed at the boiling point by ammonia. Or the Rutile may be fused with six parts of bisulphate of potassa, until there is complete solution, treated with cold water, and the titanic acid precipitated by long boiling, on the addition of some sulphite of soda.

Titaniferous iron can be treated in a similar way.

Titanite is decomposed by gentle red heat, being mixed with some bisulphate of ammonia.

8. [OXIDES OF TANTALUM, NIOBIUM, and PELOPIUM.]

These are contained in Tantalite, Yttrotantalite, and Columbite. These very similar oxides may be obtained, if the finely pulverized minerals are fused to their complete solution, along with six times their weight of bisulphate of potassa; on treatment with hot water, the acids remain behind, from which, by treatment with ammonia and sulphide of ammonium, tin and tungsten may be removed, and with chlorhydric acid, iron. The Tantalite of Finland furnishes its tantalic acid in this way, and the columbite of Bodenmais, niobic and pelopic acid. If the latter be mixed with charcoal and exposed to a red heat in dry chlorine gas, the white infusible chloride of niobium will be first sublimed, and afterwards the yellow, fusible, and more volatile chloride of pelopium. These oxides, as hydrates, are partly soluble in caustic alkalies, but after ignition they become insoluble. The hydrates containing sulphuric acid are soluble in chlorhydric acid; if zinc be present the solution will be blue, which is brown in case of niobic acid.

Before the outer flame of the blowpipe, they dissolve in phosphate of ammonio-soda, forming a colorless bead; in the inner flame, tantalic acid forms a colorless, pelopic acid a brown, and niobic acid a blue bead. If iron be present, the last two become a blood red.

9. Oxides of Chromium.

Sesquioxide, Cr_2O_3; *Chromic acid*, CrO_3.[*] — a. The *sesquioxide of chromium* is a weak base, like the sesquioxide of iron and of aluminium. There are two different modifications of it, which are distinguished by the color of their salts; the one forming violet, and the other green salts.

Ammonia precipitates the blueish or greenish gray hydrate (Cr_2O_3, $9HO$), which is partly soluble in excess of the precipitant giving a reddish solution.

Caustic potassa, or *soda*, likewise precipitates the hydrated sesquioxide, which is readily dissolved when cold in an excess of the precipitant, giving a green color. If this alkaline solution is boiled for a long time, the sesquioxide (as Cr_2O_3, $8HO$) is reprecipitated, and the supernatant liquid becomes colorless.

Sep from

Alkaline carbonates as well as *sulphide of ammonium*, also throw down, in solution of the oxides of chromium, the hydrated sesquioxide.

The sesquioxide of chromium, after ignition, is almost entirely insoluble in acids, while on the other hand the hydrate is very soluble, forming a green or violet-blue solution which appears red by transmitted light. The sesquioxide becomes soluble on being fused along with bisulphate of potassa; and by fusion with the alkaline carbonates (especially if nitre is added) it is converted into chromic acid, which combining with the alkali, is soluble in water, giving it a yellow color.

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[*] The comportment of the other oxygen compounds of chromium, the protoxide CrO, the oxides Cr_3O_4 and CrO_2, and perchromic acid Cr_2O_7 is not treated of, since all these can be readily converted into the two given above.

This last reaction is used in examining for chromium in its native compounds (chromic iron (FeO, Cr_2O_3,) and iron ore), as well as for the complete separation of such oxides as will not be more highly oxidized by fusion with nitre (as alumina, sesquioxide of iron, magnesia, etc.), and which are insoluble in alkaline liquids.

Chrome iron is completely decomposed, if in a very finely pulverized condition it be mixed with four times its weight of bisulphate of potassa, exposed for a long time to a red heat, and then the cooled mass fused along with double its volume of a mixture of equal parts of nitre and an alkaline carbonate.

Sesquioxide of chromium and its compounds communicate to the pearl of phosphate of ammonio-soda, and borax, a beautiful emerald green color, both in the inner and outer flame of the blowpipe.

b. *Chromic acid* is scarlet, crystalline, deliquescent and soluble in water, producing an orange-yellow solution; it forms, with alkalies, soluble salts, — the neutral ones being yellow, and the acid, an orange red; these are isomorphous with the corresponding sulphates. The acid chromates of strontia, lime, and magnesia, are soluble in water, though all the other chromates of the metallic oxides are either insoluble or only slightly soluble.

The salts of baryta form, in the soluble chromates, a yellow (BaO, CrO_3), *the salts of lead* a lemon color (PbO, CrO_3), *the salts of silver* a purple-red (AgO, CrO_3), and *the subsalts of mercury* a brick-red ($4\,Hg_2O, 3\,CrO_3$) precipitate. All these precipitates are soluble in nitric acid, — the chromate of lead is also soluble in potassa. The subchromate of mercury deposits the sesquioxide of chromium at a red heat.

The chromates are decomposed on being heated with concentrated sulphuric acid, forming sulphates of the sesquioxide of chromium, oxygen being eliminated; with concentrated chlorhydric acid they form chlorine gas and a green chloride of chromium; with a mixture of chloride of sodium and sulphuric acid, they disengage chlorchromic acid $Cr O_2 Cl$ (chlorchromsäure), which is decomposed by water into chromic and chlorhydric acid.*

Chromic acid is reduced to the green sesquioxide of chromium by sulphydric and sulphurous acid, by alcohol and sugar (in the presence of a free acid), by oxalic and tartaric acid, and by any metal which (like zinc) disengages hydrogen; the same effect is produced by heating the anhydrous acid with chloride of ammonium, charcoal, or sulphur. In these reactions with sulphydric acid, sulphur will be produced; with sulphurous acid, sulphuric; with alcohol, aldehyde and acetic acid; and with oxalic acid, carbonic acid gas. If a free acid is present, all the sesquioxide will remain in solution, giving it a green color; otherwise, there is separated, in the case of reduction by sulphydric acid, a greenish gray mixture of the sesquioxide of chromium and sulphur. In consequence of this reaction, the presence of chromic acid is indicated as in examination for basic metallic oxides by means of sulphydric acid.

The insoluble chromates, such as the chromate of lead, are best decomposed by a mixture of fuming chlorhydric acid and alcohol. The chromates comport them-

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* $K O, 2 Cr O_3 + 4 S O_3 = (K O, S O_3 + Cr_2 O_3, 3 S O_3) + 3 O.$ —
$2 Cr O_3 + 6 H Cl = Cr_2 Cl_3 + 6 H O + 3 Cl.$ —
$Na Cl + K O, Cr O_3 + 4 S O_3 = (Na O, 2 S O_3 + K O, 2 S O_3) + Cr O_2 Cl.$ —
$Cr O_2 Cl + H O = Cr O_3 + H Cl.$

selves before the blowpipe flame like the compounds of the sesquioxide.

10. [Oxides of Vanadium.]

Protoxide, $V O$; *Binoxide*, $V O_2$ and *Vanadic acid*, $V O_3$.—These are found in small quantities in many ores of iron and copper, in furnace slag, in uranium-ore, and in the brown lead ore from Zimapan.

The compounds of vanadium are very similar to those of chromium, tungsten, and molybdenum, in their comportment with reagents. The salts of the binoxide are brown, green, or, when in solution, blue; the fixed caustic and carbonated alkalies throw down the greenish white hydrate, soluble in excess, with a brown color, though insoluble in ammonia.

Vanadic acid is a yellowish brown powder, soluble in the mineral acids, and scarcely soluble in water; its salts are as little precipitated as those of the oxides, by sulphydric acid, but they are reduced by it to the condition of the binoxide, as also by sulphurous acid, sugar, oxalic acid, and alcohol; the binoxide remains in solution, giving it a blue color. Both the acid and the oxides are precipitated by sulphide of ammonium as brown sulphides of the metal, which an excess of the precipitant dissolves, acquiring a brown color. Ferrocyanide of potassium gives a yellow precipitate which becomes green on exposure to the atmosphere.

Vanadiate of ammonia is insoluble in a saturated solution of chloride of ammonium; and when heated in contact with the air, vanadic acid is left behind, of a dark red color, or when exposed to greater heat the acid fuses.

The oxides of vanadium before the blowpipe, dissolve in borax and the phosphate of ammonio-soda, producing a yellow color in the outer flame, and a brown in the inner, which become chrome green on cooling, although they may either become yellow or have their color destroyed if heated again in the oxidation flame.

For the detection of vanadium (in iron ores) the pulverized ore is fused for an hour with one third of nitre in a red heat, and after it has cooled it is boiled with a little water, and the yellow filtrate (containing vanadiate, chromate, phosphate, nitrate, and silicate of potassa and alumina) is mixed with nitric acid, until the reaction is left only slightly alkaline. The alumina and silica are removed by filtration, and a precipitation is produced by excess of chloride of barium. The washed precipitate (composed of vanadiate, chromate, and phosphate of baryta) is boiled while yet moist with dilute sulphuric acid, and the reddish-yellow filtrate concentrated after it has been saturated with ammonia. On evaporating and placing a piece of chloride of ammonium in the solution, by degrees a white or yellow crystalline powder, the vanadiate of ammonia, will be separated. Or the above yellow solution is reduced by sulphurous acid, neutralized by ammonia, and the precipitated oxides digested with sulphide of ammonium, when the vanadium will be dissolved as the sulphide, from which solution it can be separated by dilute sulphuric acid; or by fusion with nitre it will be changed into a vanadiate of the alkali.

GROUP IV.

METALLIC OXIDES WHICH ARE NOT PRECIPITATED BY SULPHYDRIC ACID FROM THEIR SOLUTIONS MIXED WITH CHLORHYDRIC ACID, BUT WHICH ARE PRECIPITATED AS SULPHIDES, FROM NEUTRAL SOLUTIONS, BY SULPHYDRIC ACID AND SULPHIDE OF AMMONIUM.

Protoxide of Nickel, Cobalt, Manganese, Zinc, and of *Iron,* and *the Sesquioxide of Iron* and of *Uranium.* — The metallic oxides discussed in the last group, in neutral aqueous solutions of their salts, do not exchange their oxygen for the sulphur of sulphydric acid; they are precipitated by the action of the ammonia of the sulphide of ammonium, sulphydric acid being evolved in this reaction,[*] as oxides, which are not soluble by themselves in water or ammoniacal salts (as the alkalies and alkaline earths). (The oxides of vanadium are the only exceptions to this rule). The metallic oxides of the fourth group, also those of nickel, cobalt, manganese, zinc, iron, and uranium are decomposed, in *neutral* solutions of their salts, by sulphydric acid, with the consequent formation of water and a metallic sulphide insoluble in water, which is precipitated with a peculiar color. Since an amount of acid is set free which corresponds with the precipitating sulphide, this precipitation will never be complete, if the acid be a mineral acid; on which account, the precipitation is thoroughly effected by the sulphide of ammonium, because the ammonia of this compound neutralizes the acids of the salts.[†]

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[*] E. g. $Al_2O_3, 3\,ClH + 3\,NH_4S = Al_2O_3 + 3\,NH_4Cl + 3\,SH$.

[†] E. g. $MnO, SO_3 + NH_4S = MnS + NH_4O, SO_3$.

The metals of the oxides of this group decompose water in the presence of an acid; their sulphides under the same circumstances evolve sulphydric acid gas. The sulphide of nickel and of cobalt are with difficulty decomposed by dilute chlorhydric and acetic acid, while the sulphide of zinc is insoluble in acetic acid.

These oxides are not thrown down as sulphides by sulphydric acid, when their solutions have been mixed with a *sufficient* quantity of a mineral acid. Those which contain one equivalent of oxygen for every equivalent of metal (NiO, CoO, MnO, ZnO, and FeO) comport themselves, in their salts, with chloride of ammonium and ammonia as magnesia (MgO); they form double compounds with the salts of ammonia, which are not decomposable by ammonia; hence these metallic oxides when so situated are not precipitated by this latter reagent. But those which contain three equivalents of oxygen for every two of metal (Mn_2O_3, Fe_2O_3, Ur_2O_3) comport themselves in this particular as the isomorphous alumina (Al_2O_3) and the sesquioxide of chromium (Cr_2O_3); they are completely precipitated by ammonia, even in the presence of chloride of ammonium. The presence of tartaric acid and many other non-volatile organic compounds prevents the precipitation of these oxides by caustic and carbonated alkalies, but not their precipitation by the sulphide of ammonium. The oxides of the formula MO are neither thrown down, from the neutral solutions of their salts, by digestion in the cold with carbonate of baryta or lime, nor by heat from their solutions mixed with acetate of soda. The oxides of the formula M_2O_3 are precipitated under these circumstances.

1. Oxide of Nickel. NiO.

Nickel is found as an arsenide (Ni_2As and $NiAs$), a sulphide (NiS), a sulpharsenide (NiS_2, $NiAs_2$) and as nickel-ochre ($3\,NiO, AsO_5 + 5\,aq$), in small quantities in meteoric iron, olivine, and black oxide of manganese, mostly associated with cobalt. Nickel speiss is composed, besides nickel, mostly of copper, cobalt, manganese, bismuth, antimony, arsenic, and sulphur.

The hydrated salts of the oxide are green, the anhydrous yellow; their solutions redden litmus. The neutral salts are only *partially* precipitated by *sulphydric acid*, and when mixed with chlorhydric acid, they are *not at all* precipitated. But the *acetate of nickel*, or any other salt mixed with acetate of soda, is completely precipitated if the solution be warmed, and there is not too much free acetic acid present. The precipitated black sulphide of nickel (NiS) is with difficulty soluble in dilute chlorhydric and in acetic acid, though very soluble in nitric and nitro-chlorhydric acid.

Sulphide of ammonium likewise throws down the sulphide of nickel, of which only a very small quantity is soluble in excess of the precipitant, giving it a brown color. On this account a brown color of the liquid, (which is poured off from a precipitate produced by sulphide of ammonium,) indicates the presence of nickel.

Potassa throws down the apple-green hydrate of the oxide of nickel (NiO, HO), insoluble in excess of the precipitant, but soluble in ammoniacal salts.

Ammonia will not precipitate the acid salts of the oxide, or such as are mixed with the chloride of ammonium, and only partially precipitate those which are neutral, the precipitate being soluble in excess of ammonia. Potassa precipitates the hydrated oxide by degrees from this ammoniacal solution.

The *alkaline carbonates* throw down the basic carbonate, which precipitate, when produced by carbonate of ammonia, is soluble in excess of the precipitant.

Phosphate and *arseniate of soda* precipitate the greenish white phosphate or arseniate of nickel.

Oxalic acid gradually precipitates almost all the nickel as an oxalate, which from its solution in ammonia when exposed in an open vessel, separates sooner than oxalate of cobalt. (An imperfect method of separation from cobalt.)

Cyanhydric acid throws down all the nickel, as the cyanide ($NiCy$), from a solution of the acetate of nickel (or from any salt of the protoxide which has been mixed with some acetate of soda); *cyanide of potassium* occasions the same precipitation, readily soluble in excess of the precipitant. The solution, in the latter case, contains the double cyanide of nickel and potassium ($NiCy, KCy$), from which the cyanide of nickel is separated by dilute sulphuric or chlorhydric acid (with the disengagement of cyanhydric acid), but the cyanide can only be converted into a soluble salt of nickel by excess of acid at boiling heat.

Ferrocyanide of potassium gives a greenish white, and *Ferricyanide of potassium* a yellowish green precipitate.

The sesquioxide of nickel (Ni_2O_3) is formed, by treating with chlorine the hydrated protoxide of nickel diffused in water, or a solution of a protosalt mixed with carbonate of baryta (or the cyanide of nickel in the presence of a free alkali). Excess of dilute chlorhydric acid prevents its formation, inasmuch as it converts it into chlorine and chloride of nickel ($NiCl$). On this reaction, rests a method of separating nickel from cobalt.

The protosalts of nickel, when heated along with soda, to a red heat on charcoal, are easily reduced to a grayish metallic powder, which is magnetic. With borax they form a hyacinth-colored bead, which is a pale yellow when cold, and which, with larger quantities of borax is a dark, yellowish-brown, becoming gray and opaque in the inner flame on account of its reduction to the metallic condition. The addition of nitre, or of any other salt of potassa, changes the brown color in the outer flame to a blue or dark purple. With phosphate of ammonio-soda there is produced, both in the outer and inner flame, a dark yellow bead, which becomes almost colorless when cold.

The natural compounds of nickel with arsenic or those produced in the arts (copper-nickel, arsenical nickel, nickel, or cobalt-speiss) are fused, for analysis or for exhibition of the metal, with six times their weight of a mixture composed of equal parts of nitre and carbonate of soda (or with three times the weight of sulphur and an alkaline carbonate); the alkaline arseniate (or the double sulphide of arsenic and potassium), thus formed, is extracted by water and the remaining oxides are dissolved in chlorhydric acid (or the metallic sulphides in this acid to which some nitric acid is added by degrees). The solution is then carefully and nearly neutralized by carbonate of soda, some acetate of soda being added towards the last, and heated to ebullition when all the sesquioxide of iron will be thrown down. The filtrate then being rendered acid by chlorhydric acid, we abstract those metals which are precipitated by sulphydric acid (copper and bismuth); again filter and heat the solution in order to expel the sulphydric acid present, and precipitate the nickel and cobalt with carbonate of soda. They can be separated as shown under the head of cobalt.

Or, the compound of nickel may be dissolved in concentrated chlorhydric acid, some nitric acid being added by degrees, heated to ebullition, nearly neutralized by carbonate of soda, with the addition of some of the acetate, and (if the precipitate is not reddish brown) also of the sesquichloride of iron. It is then boiled for some time, and freed from the basic arseniate of the sesquioxide of iron by filtration. The solution, thus freed from arsenic and iron, can be treated as above.

To obtain pure nickel, from a solution of cobalt and nickel along with sesquioxide of iron, precipitation is produced gradually by the binoxalate of potassa, and then if the ammoniacal solution of the washed precipitate be exposed to evaporation, all the nickel will separate as an oxalate, and the cobalt will remain in solution with a red color. The oxalate of nickel yields the pure metal at a red heat, free from access of the air.

2. Oxide of Cobalt. $Co\,O$. $(CoONO_5)$

Cobalt is found as cobalt-speiss ($Co\,As$), cobalt-glance ($Co\,S_2, Co\,As$), cobalt-pyrites ($Co_2\,S_3$), cobalt-bloom ($3\,Co\,O, As\,O_5, 9\,H\,O$), in small quantities in meteoric iron, in black oxide of manganese, and as an almost constant companion of nickel and iron.

Oxide of cobalt is an olive-green powder, or of a rose-red color when in the condition of a hydrate; its salts are generally blue when anhydrous, or in solutions containing free concentrated acids, though their aqueous solutions are crimson.

Its salts comport themselves with *sulphydric acid* or the *sulphide of ammonium*, like the salts of nickel; the precipitated black sulphide of cobalt ($Co\,S$) is quite insoluble in sulphide of ammonium; once formed, it is with great difficulty soluble in dilute nitric and sulphuric acid, and also in acetic acid. A solution of a salt of cobalt when mixed with some acetate of soda, being warmed, is more readily and completely precipitated by sulphydric acid than a salt of nickel under like circumstances. (On this reaction depends a mode of separating cobalt and nickel from manganese.)

Ammonia, in acid solutions of the salts of cobalt or in such solutions as contain ammoniacal salts, produces only a red color, which soon passes into a brown. If this solution is excluded from the air, there will be no precipitation of the hydrated oxide of cobalt on the addition of potassa.

Caustic potassa precipitates all the cobalt as a blue basic salt, which becomes the rose red hydrate if quickly heated, the air being excluded; but on exposure to the air it becomes the olive-green hydrated oxide.

Alkaline carbonates precipitate the peach-blossom red basic carbonate, which is readily soluble in excess of carbonate of ammonia, retaining the same color, but only slightly soluble in the carbonates of soda and potassa.

Alkaline phosphates and arseniates give similar peach-blossom red precipitates, very soluble in acids.

Oxalic acid gradually precipitates the pale rose-red oxalate, soluble in ammonia.

Ferrocyanide of potassium gives a green, and *ferricyanide of potassium* a brownish red precipitate.

Cyanide of potassium (and cyanhydric acid in a solution of the acetate of cobalt) precipitates the cyanide of cobalt ($Co\,Cy, 3\,HO$), which is easily soluble in excess of the precipitant, as also in ammonia and chloride of ammonium; though on the other hand it is insoluble in water and in dilute acids. If the solution of the salt of cobalt contain free acid (so that cyanhydric acid is evolved on the addition of cyanide of potassium), and if the cyanide of cobalt, when it begins to fall, be dissolved in an excess of cyanide of potassium, and warmed for some time, then neither dilute sulphuric nor chlorhydric acid will produce a precipitate any longer in the solution, since all the cobalt has passed into the condition of cobalto-cyanide of potassium ($Co_2Cy_6, 3K$), which is not decomposable by weak acids. ($2CoCy + 3KCy + HCy = (Co_2Cy_6, 3K) + H$). If the solution of the salt contain at the same time some oxide of nickel, on the addition of chlorhydric acid (to the solution of the cyanogen compound in the cyanide of potassium) there will be produced, in every instance, a greenish precipitate which always contains all the nickel, but all the cobalt only when two equivalents of cobalt to three of nickel are present. In the latter case the precipitate is purely the cobalto-cyanide of nickel ($Co_2Cy_6, 3Ni$); in case of a larger proportion of nickel, the cyanide of nickel ($NiCy$) is mixed with this precipitate, and by long boiling along with chlorhydric acid it is decomposed into cyanhydric acid and the soluble chloride of nickel ($NiCl$). On the other hand, if the cobalt is present in larger proportion, the precipitate will consist entirely of the cobalto-cyanide of nickel ($Co_2Cy_6, 3Ni$), and some cobalt remains in solution as the cobalto-cyanide of potassium. The precipitate of the cobalto-cyanide of nickel (after the decomposition of all the cyanide of potassium and cyanide of nickel by boiling with chlorhydric acid) is converted by means of caustic potassa into the oxide of nickel (which is precipitated) and into the cobalto-cyanide of potassium.

The detection of nickel along with cobalt is accomplished in the following way; the solution, containing these two metals (free from manganese and iron), is made slightly acid by chlorhydric acid, mixed with excess of cyanide of potassium and heated to ebullition; on the addition of dilute chlorhydric or sulphuric acid, there will be a precipitate if nickel is present. A clear solution in KCy ~~then remains~~, containing the cobalt as the cobalto-cyanide of potassium, [illegible] ~~which being mixed with an~~ alkali, is saturated when cold with chlorine, and a very small quantity of nickel will then show an inky-black fluid.

For the complete (quantitative) separation of the two metals, their solution in acids, being heated, is precipitated by slight excess of caustic soda-lye, and the hydrated oxides thus obtained, being washed and while still moist, are dissolved by the aid of heat in cyanide of potassium which contains no cyanic acid (or in cyanhydric acid and potassa lye), then heated to expel any excess of cyanhydric acid, and mixed while yet warm with washed protoxide of mercury; all the nickel is precipitated (by the decomposition of the potassio-cyanide of nickel), partly as the oxide and partly as the cyanide, but after the washed precipitate has been ignited, it is entirely converted into the oxide. The cobalt left in the solution, after exact neutralization by means of nitric acid, is entirely precipitated by neutral nitrate of mercury, and the precipitate after washing and ignition is reduced by means of hydrogen.

Or; for the separation of nickel from cobalt, the alkaline solution of the two cyanogen compounds is saturated *when cold* with chlorine, and the solution is at last made strongly alkaline by caustic alkali; all the nickel is precipitated as the black sesquioxide, while the cobalt remains in the solution.

+ A solution of chloride of cobalt, mixed with much free chlorhydric acid and sufficiently diluted, will be com-

$$\left.\begin{matrix} 2\,CoCl \\ 2\,NiCl \end{matrix}\right. + 4\,Cl = \left.\begin{matrix} Co_2Cl_3 \\ NiCl \end{matrix}\right\} \text{add } 4BaOCO_2 \left\{\begin{matrix} Co_2O_3 \text{ ppt} \\ NiO \text{ sol. salt with Amm sal} \\ 4BaCl \end{matrix}\right.$$

pletely converted into the sesquichloride (Co_2Cl_3) by the long continued passage of chlorine through it, from which, carbonate of baryta throws down, in the cold, all the cobalt as the sesquioxide. Since the chloride of nickel could not be affected under these circumstances, this comportment answers likewise for the complete separation of the two metals.

Native compounds of cobalt or the products of smelting which contain it, are separated from arsenic and iron in the manner described under the head of nickel, (vide page 32).

All the compounds of cobalt dissolve in borax and phosphate of ammonio-soda before the blowpipe, forming a bead of a light or dark blue color both in the inner and outer flame; these colors are not concealed by the presence of other metallic oxides. The salts of cobalt comport themselves with soda, like those of nickel.

For the more certain qualitative proof of cobalt, we possess its comportment before the blowpipe, and the difficult solubility of its sulphide in dilute chlorhydric or in acetic acid. The smallest traces of cobalt (or nickel) can easily be detected in iron ore, in black oxide of manganese, and in other minerals, when their solutions in chlorhydric acid are first treated with sulphydric acid (in order to remove the metals which are precipitable by this reagent), and then potassa being added, they are again treated with sulphydric acid, when the sulphides of these two metals will be thrown down; these being then drenched on the filter with dilute chlorhydric acid, can be washed out and the undissolved black sulphide of cobalt or sulphide of nickel can be tested for, by the blowpipe for cobalt, and for nickel in its solution by means of cyanide of potassium, according to the method previously given. When a large quantity is present in the sesquioxide of iron, the latter is carefully removed first by boiling the solution, after it has been nearly neutralized by carbonate of soda, along with a little acetate of soda.

3. OXIDES OF MANGANESE.

Protoxide, MnO. *Sesquioxide,* Mn_2O_3. *Binoxide,* MnO_2. *Manganic acid,* MnO_3. *Permanganic acid,* Mn_2O_7. — Manganese is found as Manganese-spar (MnO, CO_2), as Silicate, as Braunite (Mn_2O_3), as Manganite (Mn_2O_3, HO), Pyrolusite (MnO_2), Hausmanite (Mn_3O_4) etc.; it is also an almost constant companion of iron.

a. *Protoxide of manganese,* MnO. The salts of this oxide are either pale red or colorless, mostly soluble in water, and all soluble in chlorhydric acid. All the higher oxides, on being heated along with chlorhydric acid, pass into the condition of the chloride ($MnCl$) which corresponds with this oxide, chlorine gas being disengaged; accordingly any compound of manganese when treated with excess of this acid always shows the reactions of the salts of the protoxide. These do not repass into the condition of salts of the sesquioxide on exposure to the air, or on boiling their aqueous solutions with nitric acid.

Sulphydric acid occasions no precipitate with the protosalts of manganese, not even with the acetate; *sulphide of ammonium* gives a flesh-colored precipitate of the sulphide of manganese (MnS) which is readily soluble in acetic acid, and which becomes a brownish-red on exposure to the air (on account of its absorption of oxygen). When the quantity of manganese is small, and the reaction has presented a yellow color on account of the use of the pentasulphide of ammonium, the precipitate often appears by degrees, at first of a yellowish-white, becoming a flesh-color on standing.

Caustic potassa or soda precipitates the white hydrate of the protoxide, insoluble in excess of the precipitant, becoming quickly brown on exposure to the air, and then no longer completely soluble in chloride of ammonium.

Ammonia, in acid solutions of the protosalts or in those which contain ammoniacal salts, gives no precipitate at first; but the solution becomes turbid on exposure to the air and deposits (if sufficient ammonia be used) all the metal as the brown hydrate of the sesquioxide.

Alkaline carbonates, phosphates, arseniates, and *oxalates* occasion white precipitates.

Ferrocyanide of Potassium gives a white precipitate with the protosalts, and *ferricyanide of Potassium* a brownish yellow. If the peroxide of lead (or minium) be heated with excess of nitric acid, and a trace of a protosalt of manganese happens to be present (or if the fluid is to be tested for manganese), the fluid assumes the intense purple-red color of permanganic acid, which is very perceptible after the deposition of the excess of binoxide. (A delicate test for manganese.)

b. *Sesquioxide of manganese,* Mn_2O_3. The salts of this oxide are of an intense columbine-red (columbinroth) color, and pass into the condition of protosalts, with a loss of color, when in contact with reduction agents (chlorhydric, sulphurous, and nitrous acid, organic matter, etc.), or when heated by themselves. If an oxide, or if a salt of manganese which is decomposable by heat, be exposed to an intense ignition in the air, the red oxide is produced $Mn_3O_4 = MnO, Mn_2O_3$; and if this is ignited in contact with a metallic oxide of the formula MO, the sesquioxide Mn_2O_3 will be produced.

c. *Binoxide of manganese*, MnO_2. This is the most important native compound of manganese. When anhydrous, it is a grayish-black powder, or when a hydrate, brown. It disengages oxygen, when ignited by itself, or when heated along with sulphuric acid; chlorine is evolved when chlorhydric acid is used, and carbonic acid, if oxalic acid is present.* It is precipitated as the brown hydrate (MnO_2, HO), when any protosalt of manganese is mixed with a hypochlorite. Its solution in chlorhydric acid comports itself after it has been heated, like a protosalt.

d. *Manganic acid*, MnO_3. This compound only exists in combination with alkalies, forming with them intense blueish-green salts. It is formed whenever any compound of manganese is fused with excess of caustic or carbonated alkali; its formation is favored by the addition of nitre. Its green solution becomes red on exposure to the air, or by the addition of nitric acid, on account of the formation of permanganic acid, and the deposition of the binoxide, and it comports itself as these two; $3(KO, MnO_3) = KO, Mn_2O_7 + MnO_2 + 2KO$. One of the most delicate methods of detecting manganese rests on the formation of a green alkaline manganate. The substance to be examined for manganese is fused on platinum foil with *excess* of carbonate of soda, and some nitre; a bluish-green color in the fused

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* $3MnO_2 = Mn_3O_4 + O_2$.
$MnO_2 + SO_3, HO = MnO, SO_3, HO, + O$.
$MnO_2 + 2HCl = MnCl, 2HO + Cl$.
$MnO_2 + 2C_2O_3 = MnO, C_2O_3 + C_2O_4$.

mass indicates manganese. To test small quantities of manganese in minerals rich in iron, the iron is first removed by boiling the solution containing the oxides, after it has been nearly neutralized by carbonate of soda, and mixed with some acetate of soda; then super-saturate with ammonia, decompose by a few drops of sulphide of ammonium and test the precipitate, thus formed, by fusion along with carbonate of soda and nitre, on platinum foil. If the fused mass is brown, too little nitre, or too much of the substance, to be examined, has been used.

e. *Permanganic acid,* Mn_2O_7. See its formation, under manganic acid. Its salts dissolve in water with an intense purple-red color, which is immediately decolorized by organic materials, and all the reduction agents (chlorhydric, sulphurous, arsenious, nitrous, and sulphydric acid, protosalts of iron, etc.) On its formation depends the delicate method already mentioned (page 39), for the detection of manganese by means of nitric acid and the peroxide of lead.

A method for the quantitative determination of iron depends on the decolorization of permanganic acid, in a dilute titrited solution, by the protosalts of iron.

All the compounds of manganese give amethystine-red beads, along with borax, and the phosphate of ammonio-soda, in the outer flame of the blowpipe, and bluish-green beads, with soda, in the oxidation flame.

Manganese is easily separated from cobalt and nickel, by means of sulphydric acid, which is admitted into the warm solution, containing not too much free acid, and mixed with acetate of soda; the latter metals are precipitated, while the former remains in solution. Or the oxides are converted into sulphides by being heated in a stream of sulphydric acid gas, and these then being treated with cold dilute chlorhydric acid, the manganese is alone taken up in solution.

4. Oxides of Iron.

FeO, SO,

Protoxide, FeO; *Sesquioxide*, Fe_2O_3; *Ferric acid*, FeO_3. Iron is largely distributed in the three kingdoms of nature; rarely native, mostly in combination with oxygen, sulphur, or arsenic, or as different salts of the protoxide or sesquioxide.

a. *Protoxide of iron*, FeO. The salts of this oxide are formed by dissolving the metal in a dilute acid; as hydrates, they are bluish-green, or when anhydrous, white. They oxidize gradually on exposure to the air, forming a salt of the yellow basic oxide, which is deposited in a neutral solution. They give up their acids at a red heat, and a brownish-red sesquioxide is left behind. By means of nitric acid, their solutions, at the boiling point, are readily and completely converted into salts of the sesquioxide, or by means of chlorine, hypochlorous acid, or the chlorate of potassa and chlorhydric acid, without the application of heat. A dark-brown color is first produced when nitric acid is employed, since some nitric oxide is dissolved along with a portion of the protosalt; on the addition of more nitric acid, this compound is decomposed, the nitric oxide being disengaged, and the solution possesses the color of the sesquisalts.*

Sulphydric acid gives no precipitate in acid solutions of the protosalts; the acetate is only partly precipitated.

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* In order to prevent the separation of the basic salt of the sesquioxide, only half as much acid as the neutral protosalt already contains must be added to the solution.

Sulphide of ammonium throws down the iron completely as the sulphide (FeS), which is slightly soluble in excess of the precipitant, when much carbonate of soda is present. The sulphide oxidizes very quickly, in the air, becoming a brownish-red basic sesquisalt; it can be washed out, without decomposition, by water, free from air, containing a few drops of sulphide of ammonium; it is readily soluble in chlorhydric acid, sulphydric acid being evolved, and it is converted into the chloride of iron ($FeCl$).

Caustic alkalies precipitate the white hydrated protoxide, in solutions which contain no sesquioxide; it becomes quickly a dirty green, and at last a reddish brown; *alkaline carbonates* and *phosphates* produce similar effects.

Ferrocyanide of potassium forms a white precipitate, or with solutions containing small quantities of the sesquioxide, a bluish white ($2\,Cfy, Fe_3K$), which is quickly converted into Prussian blue ($3\,Cfy, 4\,Fe$) on exposure to the air or any oxidizing agent. The recently precipitated compound, on the addition of potassa, separates, from the hydrate of the sesquioxide which has become blue, the hydrated protoxide.

Ferricyanide of potassium gives immediately, with the protosalts, a beautiful blue precipitate ($2\,Cfy, 3\,Fe$). The last two precipitates are insoluble in chlorhydric acid, and they cannot be produced in alkaline solutions, since they are decomposed by alkalies.

Tincture of galls gives no precipitate with protosalts, if they contain no sesquioxide of iron.

The protosalts reduce the *chloride of gold*, and *nitrate of silver* to the metallic condition.

b. *Sesquioxide of iron*, Fe_2O_3. This is a reddish-brown powder, unchanged when ignited by itself. It is completely soluble in chlorhydric acid (that which is native or which has been ignited being only slowly soluble); the solutions of the sesquioxide of iron are brownish red or yellowish brown, and are completely decomposed by boiling if they are dilute and as neutral as possible, the sesquioxide being separated; if phosphoric or arsenic acid be present, these acids will be contained in the precipitate. By being heated along with *metallic iron* or with *sulphurous acid*, or by the passage of *sulphydric acid* through their solutions, the sesquisalts are reduced to the condition of protosalts; in the latter case there is a separation of the sulphur which renders the fluid milky.*

The sesquisalts comport themselves with the *sulphide of ammonium* like the protosalts; sulphur is however mixed with the precipitated sulphide of iron, but it is left behind on dissolving the precipitate in chlorhydric acid.

Caustic and *carbonated alkalies*, also *ammonia* and *the carbonate of ammonia* precipitate the sesquioxide of iron as a reddish-brown hydrate (Fe_2O_3, $2HO$), containing some alkali, which is quite insoluble in excess of the precipitant, also in the presence of ammoniacal salts. The non-volatile organic compounds (tartaric acid, sugar) prevent this precipitation, though they do not affect that produced by sulphide of ammonium.

The carbonates of the alkaline earths throw down the sesquioxide completely, even in the cold, (which serves to separate Fe_2O_3 from FeO, MnO, etc.).

Phosphate and *arseniate of soda* precipitate the white phosphate or arseniate of the sesquioxide (serving for

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* $Fe_2O_3, 3SO_3 + Fe = 3(FeO, SO_3)$.
$Fe_2O_3, 3SO_3 + SO_2 = 2(FeO, SO_3) + 2SO_3$.
$Fe_2O_3, 3SO_3 + HS = 2(FeO, SO_3) + SO_3, HO + S$.

the separation of the phosphates of the alkaline earths) insoluble in acetic acid, though soluble in the sesquiacetate of iron, also in ammonia, if an excess of phosphate of soda is present.

Ferrocyanide of potassium produces Prussian blue (3 Cfy, 4 Fe), insoluble in chlorhydric acid, which is resolved by caustic potassa into the hydrated sesquioxide of iron and the ferrocyanide of potassium; $3\,(\mathrm{Cfy}, 2\,\mathrm{K}) + 2\,(\mathrm{Fe_2O_3}, 3\,\mathrm{SO_3}) = 3\,\mathrm{Cfy}, 4\,\mathrm{Fe} + 6\,(\mathrm{KO}, \mathrm{SO_3})$.

Ferricyanide of potassium produces no precipitate, but only a dark color.

Tincture of galls precipitates the sesquisalts of iron of a blue black; *succinate* and *benzoate of ammonia*, in neutral solution, throw them down completely, of a reddish brown; *sulphocyanide of potassium* produces a blood-red color, which is not destroyed by chlorhydric acid.

The protoxide is present together with the sesquioxide in forge scales, and in magnetic iron ($\mathrm{Fe_3O_4}$); their solution in chlorhydric acid comports itself as a mixture of both these oxides; they are precipitated black by potassa and ammonia.

c. *Ferric acid,* $\mathrm{FeO_3}$. This is formed under similar circumstances to manganic acid; it is only known in combination with alkalies, and forms with them beautiful red solutions, which are reduced (the hydrated sesquioxide being precipitated) more easily than the manganates.

The oxides of iron impart a brownish or yellowish red to borax and phosphate of ammonio-soda, in the outer flame of the blowpipe, and a green in the inner flame, which color nearly disappears on cooling.

The search after, and recognition of iron, even in the presence of all the other bases, is accompanied with no difficulty; its precipitation as the sesquioxide by ammonia, even in the presence of ammoniacal salts, the blue precipitates (insoluble in chlorhydric acid, and decomposable by potassa) which the ferrocyanide of potassium produces in solution of the sesquioxide, and ferricyanide, in that of the protoxide, sufficiently characterize it; the two latter reactions, moreover, serve to distinguish between the two oxides. For the complete separation of the two oxides, their solution in chlorhydric acid is digested with carbonate of baryta or lime, free from contact of the air, when the sesquioxide is precipitated, and the protoxide remains in solution.

Iron can be easily and perfectly separated from the *alkalies*, from *baryta*, *strontia*, and *lime*, as the sesquioxide, by means of chloride of ammonium and ammonia; from *magnesia*, and from the *protoxide of manganese*, *nickel*, or *cobalt* it is more certainly separated if the dilute solution holding it as a sesquioxide is mixed first with carbonate of soda, until the fluid becomes reddish brown, and then with some acetate of soda; on heating to ebullition, the sesquioxide of iron is alone precipitated. If there are only small quantities of manganese, magnesia, or lime present, the acid solution is diluted with much water, and carbonate of soda is gradually added, drop by drop, with constant stirring, until all the sesquioxide is precipitated; the other bases remain dissolved in the free carbonic acid.

Sesquioxide of iron is separated with difficulty and imperfectly from *alumina*, by boiling with caustic potassa-lye, — this is effected more easily if the acid solution is first heated to ebullition along with some sulphite of soda, then neutralized with carbonate of soda and boiled with excess of soda-lye until the precipitate is black and powdery; or the precipitate produced by sulphide of ammonium is boiled along with caustic alkali with the addition of the sulphide until the fluid which was at first green, deposits by standing, black flakes, and then appears yellow.

Small quantities of sesquioxide of chromium are insoluble in caustic alkali, if much sesquioxide of iron be present; but on the other hand, small quantities of sesquioxide of iron are soluble in caustic alkali, if much sesquioxide of chromium be present. On this account, the sesquioxide of iron is separated from that of chromium more accurately than by means of caustic alkali, by fusing with nitre and an alkaline carbonate, and lixiviating with water. For the separation of the sesquioxide from titanic acid, see page 21, from phosphoric acid, see above.

All the compounds of iron occurring in nature are soluble in concentrated chlorhydric acid (and if the solution be not effected by it alone, it will be produced by the addition of some nitric acid); iron slag (the silicate of the protoxide) is completely decomposed by chlorhydric acid. The silicates of the protoxide which cannot be decomposed by acids, should be previously fused with three or four times their weight of carbonate of soda-potassa. For the determination of the mixed substances which exist in pig iron, the residue left behind on dissolving the iron in dilute sulphuric acid is employed; it commonly contains silica, carbon, carbide of iron, phosphide and arsenide of iron, chromium, vanadium, molybdenum, and sometimes also cobalt.

5. Oxide of Zinc. ZnO.

Zinc is found as an oxide in combination with silicic and carbonic acid (Calamine), and as a sulphide (Blende).

Zinc burns on being heated in the air, forming a yellow oxide, very luminous when heated, becoming white when cold. It is soluble in acids and in caustic alkalies with the evolution of hydrogen gas. All its compounds are soluble in chlorhydric acid. (Blende is soluble in aqua-regia.) Its salts are colorless, and, for the most part, yield their acids on ignition, leaving the oxide behind.

Neutral salts of the oxide are partly thrown down by *sulphydric acid*, but are not affected if they are acidified by a *sufficient* quantity of chlorhydric acid, though the acetate of zinc (or a solution of zinc mixed with acetate of soda) is *completely* precipitated by the reagent as the white sulphide (ZnS), which is insoluble in caustic alkali. *Sulphide of ammonium* produces this precipitation; the supernatant liquid is free from zinc.

Caustic alkalies, also *ammonia*, and *the carbonate of ammonia* give bulky white precipitates (the hydrate ZnO, HO or the basic carbonate), which are readily soluble in excess of the precipitant, and in chloride of ammonium; from which solution sulphydric acid precipitates the sulphide of zinc.

Carbonate of soda throws down (at the boiling point, and in the absence of chloride of ammonium) all the oxide as the basic carbonate ($8\,ZnO, 3\,CO_2, 6\,HO$), insoluble in excess of the precipitant.

Phosphate of soda, *oxalic acid*, and *ferrocyanide of potassium* also throw down white precipitates in solutions of the protosalts of zinc.

Ignited with soda on charcoal, the salts of the oxide of zinc give an incrustation of the oxide, which is yellow and not volatile when heated, becoming white when cold; moistened with nitrate of cobalt, and strongly ignited, there will be a green residue; they dissolve in phosphate of ammonio-soda, and form colorless, transparent beads, which appear enamelled, on becoming cold, if much of the oxide is present.

The oxide of zinc is easily detected, and distinguished from other oxides. Its solubility in ammonia and caustic potassa, and its precipitation from these solutions by sulphydric acid, and non-precipitation by chloride of ammonium, distinguish it from alumina, and the other oxides which are soluble in potassa. It is separated from the alkalies and alkaline earths by sulphide of ammonium, from alumina, glucina, and sesquioxide of chromium in potassa-solution, by sulphydric acid, or from their solution in acids, by chloride of ammonium and ammonia, the oxide of zinc being left in the solution. It is imperfectly separated from the sesquioxide of iron, by chloride of ammonium and ammonia, or by boiling the solution, mixed almost to neutralization with carbonate of soda, along with acetate of soda; but more perfectly by precipitating the sesquioxide of iron with an alkaline succinate; from the protoxide of manganese by hypochlorite of soda, as well as by sulphydric acid in an acetic acid solution; from the protoxides of nickel and cobalt imperfectly by boiling with caustic potassa,—more perfectly separated from nickel (in Argentan), since the latter is reduced to a metallic condition when a mixture of the oxides is heated in hydrogen gas, (or from the oxalate of nickel by ignition under exclusion of the air,) and the oxide of zinc is then removed by digestion in a concentrated solution of the carbonate of ammonia; or the freshly precipitated oxides are treated with potassa-lye and cyanhydric acid, until they are completely dissolved, and then decomposed with protosulphide of potassium, which precipitates only the zinc; after boiling the filtrate with aqua-regia, the oxide of nickel is precipitated by caustic potassa.

6. [Oxides of Uranium.]

Protoxide, U O and *Sesquioxide,* U_2O_3. Uranium is only of rare occurrence, found as the impure proto-sesquioxide (in Uranium-pitch), as the hydrated oxide (in Uranium-ochre), as phosphate of uranium, of copper, and of lime, (in Uranium-mica and Uranite).

a. *Protoxide of Uranium,* U O. This arises when the protoxalate is ignited in hydrogen gas; its salts are green and are readily converted into those of the sesquioxide on exposure to the air, or on the addition of nitric acid.

b. *Sesquioxide of Uranium,* U_2O_3. When existing as a hydrate it is a lemon-yellow color, or, when anhydrous, of a brick red; when ignited, it becomes the dark olive-green proto-sesquioxide (U_3O_4). Its salts are soluble in water, or in acids, giving a yellow color to the solutions; they mostly contain an equivalent of acid for each equivalent of the sesquioxide.

Sulphydric acid produces no precipitate, if free chlorhydric acid be present; *sulphide of ammonium* precipitates the brownish-black sulphide of uranium, which is deposited very slowly.

Caustic alkalies, as well as *ammonia,* throw down an orange-yellow compound of the sesquioxide with the alkali (Uranoxyd-Alkali), which is insoluble in excess.

Alkaline carbonates give a pale yellow precipitate, which is soluble in excess especially of carbonate of ammonia, though it is again precipitated from such a solution by boiling.

Ferrocyanide of potassium gives a lively reddish-brown precipitate, which is resolved by caustic potassa into the ferrocyanide of potassium, and the lemon-yellow compound of the sesquioxide of uranium with the alkali (Uranoxydkali).

Phosphate and *arseniate of soda, succinate of ammonia,* and *oxalic acid* give yellow precipitates.

The sesquioxide of uranium gives a green color to fluxes in the inner flame, which becomes yellow in the outer.

The sesquioxide is recognized on account of the precipitation produced by sulphide of ammonium, by potassa, and by ammonia, (even in the presence of chloride of ammonium,) and by its solubility in carbonate of ammonia, by which it is separated from the sesquioxide of iron.

For the determination of sesquioxide of uranium in Uranium-pitch (UO, U_2O_3), which usually contains silicic acid, iron, nickel, cobalt, zinc, copper, bismuth, lead, manganese, arsenic, antimony, sulphur, lime, and magnesia, and sometimes, also, selenium, and vanadium,—being pulverized finely, it is digested with moderately dilute sulphuric acid, with the addition of some nitric acid, then, most of the excess of acid being evaporated, digested with water and the white residue (consisting of silicic acid, sulphate of lead, and the basic sulphate and arseniate of bismuth) removed by filtration. The solution, being heated to 60° or 70° C., is then saturated with sulphydric acid, and, being suffered to stand for twenty-four hours, the precipitate, after the evaporation of the gas, is removed by filtration; it consists of sulphide of arsenic, antimony, copper, lead, and of bismuth. The filtrate is now heated to the boiling point, and nitric acid added (in order to sesquioxidize the iron) until its color is decidedly yellow, when it is precipitated by excess of ammonia and filtered. The precipitate contains the sesquioxide of uranium and of iron, together with a small quantity of nickel, cobalt, zinc, magnesia, and lime; the other portion of these latter metals is contained in the filtrate. After washing, the precipitate is digested with a concentrated solution of carbonate of ammonia, until it appears like the hydrated sesquioxide of iron, it is then filtered warm and suffered to cool, when the pure carbonate of the sesquioxide of uranium-ammonia is deposited. The mother liquid being then mixed drop by drop with sulphide of ammonium, so long as a blackish-brown precipitate is produced (sulphides of cobalt, nickel, and zinc), which is immediately filtered off; and the filtrate deposits all its sesquioxide of uranium by long boiling.

For the complete separation of the hydrated sesquioxide of iron from the sesquioxide of uranium united with it, the compound is dissolved in the smallest quantity of chlorhydric acid, neutralized with carbonate of ammonia, and this solution dropped into a mixture of carbonate of ammonia and sulphide of ammonium, which being stirred, all the iron as a sulphide is precipitated, the sesquioxide of uranium remaining in solution.

Selenium and vanadium are found in Uranium-pitch, by ignition along with a fourth of its weight of nitre, and carbonate of soda, from which water will extract the seleniate, vanadiate, and arseniate of alkali.

GROUP V.

METALS, WHOSE SULPHUR COMPOUNDS ARE INSOLUBLE IN DILUTE MINERAL ACIDS, AND WHICH CAN BE COMPLETELY PRECIPITATED FROM SOLUTIONS, ACIDIFIED WITH EITHER CHLORHYDRIC OR NITRIC ACID, BY SULPHYDRIC ACID.

This group is divided into two sections, as follows:—

1. Metals, whose oxygen and sulphur compounds possess the character of *bases; Lead,* Pb; *Silver,* Ag; *Mercury,* Hg; *Bismuth,* Bi; *Copper,* Cu; *Cadmium,* Cd; *Palladium,* Pd; *Rhodium,* Rh; *Osmium,* Os; *Ruthenium,* Ru.

The sulphides of these metals are not soluble in soluble basic sulphides, (as the sulphide of potassium, and of ammonium).

2. Metals, whose higher oxygen and sulphur-compounds possess the character of *acids; Antimony,* Sb; *Arsenic,* As; *Tin,* Sn; *Gold,* Au; *Platinum,* Pt; [*Iridium,* Ir; *Selenium,* Se; *Tellurium,* Te; *Molybdenum,* Mo; *Tungsten,* Wo; and *Vanadium,* Va]. Their sulphides are soluble in sulphide of potassium or of ammonium, and they form, in this way, sulphur salts, which correspond for the most part with their oxygen salts.

The metals of these two sections are separated according to these peculiarities; their solution being acidulated with chlorhydric or nitric acid, is completely precipitated by sulphydric acid (usually the liquid is warmed) and then the precipitate is treated with excess of sulphide of potassium or of ammonium; the sulphides of the first section remain undissolved, while those of the second are dissolved, and can be precipitated from this solution by dilute chlorhydric acid, with evolution of sulphydric acid; (for example, $SbS_5, 3KS + 3HCl = SbS_5 + 3KCl + 3HS$). If the sulphide of ammonium used holds one of the higher sulphides in solution, the precipitate, produced by acids, is moreover mixed with sulphur.

I. THE METALLIC OXIDES OF THE FIRST SECTION OF THE FIFTH GROUP.

1. Oxides of Lead.

Protoxide, PbO and *Binoxide*, PbO_2. — Lead is mostly found as a sulphide (Galena) or as an oxide in combination with various acids.

Protoxide of lead (PbO) is formed, as a yellow powder, when the metal is melted in the air, becoming darker every time it is heated. The nitrate and carbonate, on ignition, yield the pure oxide. This is somewhat soluble in perfectly pure water, but is quite insoluble in water containing carbonic acid, sulphates or the metallic chlorides. Its salts are mostly colorless, and those which are soluble redden litmus paper.

By *sulphydric acid*, and *sulphide of ammonium*, it is precipitated as the black sulphide of lead (PbS), insoluble in dilute acids, in potassa, and in sulphide of ammonium. This precipitate is brown or red in the presence of very much free chlorhydric acid. Insoluble salts of lead are converted, by digestion with sulphide of ammonium, into the sulphide (the acid which was united with the oxide can be detected in the filtrate, if it is not decomposable by sulphide of ammonium, as is the case with chromic acid).

Chlorhydric acid, or the soluble *metallic chlorides* precipitate, from solutions of the protosalts which are not too dilute, the white crystalline chloride of lead ($Pb\,Cl$), soluble in much water, and in strong chlorhydric acid, especially on being warmed; less soluble in dilute chlorhydric acid, insoluble in alcohol, and unchanged by ammonia.

Sulphuric acid or the soluble *sulphates* precipitate the white sulphate of lead ($Pb\,O,\ S\,O_3$), with much difficulty soluble in water, still less soluble in dilute sulphuric acid, decomposable by hot concentrated chlorhydric acid, soluble in caustic potassa, also in tartrate of ammonia with excess of ammonia, from which latter solution it can be precipitated by sulphide of ammonium or chromate of potassa; by being boiled with carbonate of soda it is completely converted into the carbonate of lead.

Chromate of potassa throws down the yellow chromate; the soluble *phosphates*, *arseniates*, and *oxalates* precipitate the corresponding white salts of lead, which are with difficulty soluble in dilute nitric acid, but soluble in much caustic potassa.

Ammonia throws down, after some time, from the acetate of lead, the white basic salt, which is insoluble in excess of the reagent.*

The fixed *caustic alkalies* precipitate the white hydrated protoxide, soluble in great excess of alkali, especially when heated.

The *alkaline carbonates* precipitate the white carbonate (which is, when heated, $3\,Pb\,O,\ 2\,C\,O_2,\ H\,O$, or in the cold $Pb\,O,\ C\,O_2$), which is insoluble in excess of the reagent.

Ferrocyanide of potassium gives a white precipitate, ($Cfy,\ 2\,Pb$).

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* This precipitate is a hexacetate of lead, according to Normandy.
L. H. S.

Binoxide of lead (PbO_2) is found in Minium ($2PbO, PbO_2$), along with the protoxide, and is left behind when this substance is treated with nitric acid; it is thrown down along with the chloride, if a salt of the protoxide is mixed with hypochlorite of soda; along with chlorhydric acid it disengages chlorine, at the same time the chloride of lead is formed. It absorbs sulphurous acid very easily, and forms PbO, SO_3.

All the compounds of lead, when melted along with soda, or the cyanide of potassium, on charcoal, yield a ductile metallic globule and a yellow coating of the binoxide.

Galena (PbS), in the state of fine powder, being digested with fuming nitric acid, is wholly converted into sulphate of lead; the filtrate, diluted with water, contains it mixed with other metals (copper, silver, and iron). With more dilute nitric acid, a mixture of the sulphate and sulphur is obtained along with some dissolved nitrate of lead.

White lead (Bleiweiss) when treated with nitric acid, leaves behind a somewhat mixed compound of sulphate of lead and sulphate of baryta; the latter are separated by tartrate of ammonia, with an excess of ammonia, which leaves the sulphate of baryta.

Chromate of lead (commercial chrome yellow) should be first treated with a large quantity of water (for the removal of the gypsum), then with dilute nitric acid (for the removal of chalk), then with tartrate of ammonia and free ammonia (for the removal of the sulphate of lead). The remaining mixture of the chromate of lead, sulphate of baryta and clay is treated with fuming chlorhydric acid and alcohol, and the chloride of lead and of chromium removed by boiling with water; the insoluble matter (BaO, SO_3 and clay) being heated with concentrated sulphuric acid, is then extracted with water and the alumina precipitated by means of ammonia. Silicic acid is separated from the sulphate of baryta by boiling with carbonate of soda, and is precipitated from the filtrate by chloride of ammonium.

Binoxide of lead is separated from all the metallic oxides of the previous groups, in acid solutions by sulphydric acid, and from such as form sulphates which are very soluble, also by the action of sulphuric acid.

2. Oxide of Silver. AgO.

Silver is found native, as vitreous silver (Glaserz) (AgS), as Hornsilver, (AgCl), as Ruby ore (Rothgültigerz) ($3AgS, SbS_3$), and it is an almost constant companion of lead in galena. Nitric acid is the solvent of the metal. The oxide of silver forms colorless salts, which yield the metal on ignition.

Sulphydric acid, and *sulphide of ammonium* precipitate, from solutions of the protosalts, the black AgS.

Chlorhydric acid and the soluble metallic *chlorides* throw down the white curdy chloride of silver (AgCl), which becomes violet on exposure to the light; it is very soluble in ammonia, in cyanide of potassium, and in hypochlorite of soda, though insoluble in nitric acid; it is slightly soluble in hot concentrated nitric acid, and chlorhydric acid.

Cyanhydric acid throws down the curdy cyanide of silver (AgCy), soluble in ammonia, cyanide of potassium, and strong nitric acid.

Iodide of potassium precipitates the yellow iodide of silver (AgI), scarcely soluble in ammonia.

Caustic potassa precipitates the brown oxide of silver

(AgO). *Ammonia* affords no precipitate with a solution of the nitrate of silver containing any free acid; *the alkaline carbonates* throw down the white carbonate and *phosphate of soda,* the yellow phosphate ($3AgO, PO_5$), which are soluble in ammonia, and in nitric acid.

Some of the metals (such as zinc, iron, and copper), the sulphate of iron (or perhaps still better, the protacetate of iron), chloride of tin, sulphurous acid, and many organic compounds precipitate silver in a metallic form from its solutions.

All the compounds of silver give white shining metallic spangles, when ignited with soda on charcoal, without any incrustation.

The chloride is the form, in which silver is determined in almost all cases, and separated from other metals; its insolubility in acids, and solubility in ammonia distinguish it readily from all the other chlorides, which are insoluble, or with difficulty soluble. Silver is especially separated from lead by cupellation, or it is removed by chlorhydric acid from the *very dilute* nitric acid solution of the two which has been heated nearly to the boiling point, or it is precipitated from the nitric acid solution, by cyanhydric acid, as the cyanide of silver, or both are precipitated by carbonate of soda, and then digested with cyanide of potassium, whence the silver is taken up in solution, and can afterwards be precipitated, by nitric acid, as the cyanide of silver.

3. Oxides of Mercury.

Suboxide, Hg_2O, and *Protoxide,* HgO. — Mercury is found as a sulphide (Cinnabar), and sometimes native. Nitric acid and aqua-regia are its solvents; its solution in the former acid contains (when the metal is in excess) the suboxide,—that in aqua-regia, the chloride corresponding to the protoxide.

a. *Suboxide of mercury* is a blackish-brown powder, insoluble in water and chlorhydric acid, and is readily decomposed with the separation of the metal; its neutral salts are mostly colorless; those which are basic are yellow.

Sulphydric acid, and *sulphide of ammonium* precipitate the subsulphide (Hg_2S), which immediately separates of a black color, although but a small quantity of the precipitant be used; it is insoluble in sulphide of ammonium and in nitric acid, though very soluble in aqua-regia.

Chlorhydric acid, and the soluble *metallic chlorides*, precipitate the white pulverulent subchloride of mercury (Hg_2Cl), even in very dilute solutions, which immediately becomes black on the addition of caustic potassa or ammonia.

Potassa and *ammonia* give black precipitates of the suboxide, or of the basic salts.

Phosphate of soda, *oxalic acid*, and *ferrocyanide of potassium* give white precipitates, *ferricyanide of potassium* reddish brown, *iodide of potassium* greenish yellow, and *chromate of potassa* brick red.

Protochlorite of tin at first throws down the white subchloride, which, with excess of the reagent, passes over into gray metallic mercury.

By boiling along with nitric acid, all the subsalts of mercury are converted into protosalts.

b. *Protoxide of mercury* is an orange-yellow or brick-red powder, resolved at a red heat into the metal and oxygen gas, but little soluble in water, though readily so in chlorhydric, nitric, and cyanhydric acid. Its neutral salts are colorless,—those which are basic, are yellow.

Sulphydric acid, and *sulphide of ammonium, added in small quantities,* give a white precipitate which is a compound of the sulphide of mercury with the undecomposed salt of mercury (ex. gr. $2HgS, HgCl$); with larger quantities of these precipitants, this precipitate is gradually converted into the sulphide (HgS), first of a dingy brownish red, and then becoming black. The protosulphide is insoluble in sulphide of ammonium, in chlorhydric and nitric acid (wherein it differs from all the other metallic sulphides), but is readily soluble in aqua-regia.

Caustic potassa precipitates the yellow protoxide,—the precipitate is a brownish-red oxychloride, if there is an insufficient quantity of the potassa; *alkaline carbonates* throw down the reddish-brown basic carbonate; *ammonia* produces a white amid-compound (for example, in excess of corrosive sublimate, $3HgCl, HgNH_2$, or if the ammonia be in excess, $HgCl, HgNH_2$); *carbonate of ammonia* comports itself in like manner, and also the fixed, caustic and carbonated alkalies, in the presence of ammoniacal salts.

The cyanide of mercury ($HgCy$) is not decomposed by alkalies, though it may be by sulphydric acid.

Chlorhydric acid gives no precipitate with the protosalts, which serves to distinguish them from the subsalts.

Iodide of potassium throws down the cinnabar-red iodide (HgI), soluble in excess either of the protosalts or the reagent.

A small quantity of *protochloride of tin* throws down (in solutions of corrosive sublimate) the white subchloride of mercury; an excess, at the boiling point, throws down all the mercury in a metallic condition, which, after decanting the supernatant liquid, may be united into little globules by digestion with concentrated chlorhydric acid.

Copper, iron, and zinc separate the mercury, in a metallic condition, from all its soluble compounds (provided they do not contain too much nitric acid); this shows, on bright copper, a grayish stain, acquiring a metallic lustre on being rubbed, and disappearing by the application of heat.

All the compounds of mercury, without exception, when mixed with pulverized soda, moistened with a drop of water, and ignited in a glass tube, are resolved into metallic mercury, which is deposited in small globules in the cool portion of the tube (recognizable by the microscope when but small quantities are present). The detection of mercury in this way is easy and sure. The volatility of all its compounds, the insolubility of its sulphide in strong nitric acid (when free from chlorhydric); distinguish mercury from any other metal.

The suboxide is separated from the protoxide by means of chlorhydric acid, and the latter oxide can be detected in the filtrate by means of sulphydric acid, chloride of tin, or metallic copper.

Chloride of silver is easily separated from the subchloride of mercury by means of ammonia, in which the former is soluble, and the latter is only blackened; or they may be treated with aqua-regia, by which the subchloride is converted into the soluble chloride. The subchloride is separated from chloride of lead by employing a large quantity of hot water, in which the latter is soluble. Silver is more perfectly separated from a solution (containing mercury as a protoxide) by means of chlorhydric acid or chloride of sodium, but in the latter case, acetate of soda must be added, so as to prevent the chloride of silver from retaining some of the mercury. Or the silver can be precipitated, as a cyanide, from a solution of the nitrates, by cyanhydric acid; the solution also may be neutralized with potassa, decomposed with excess of cyanide of potassium, and then nitric acid be added, when the cyanide of silver is thrown down, and the cyanide of mercury remains in solution, in which it can be decomposed by sulphydric acid. The protoxide of mercury is separated from the protoxide of lead by precipitating both with carbonate of soda, and then digesting with cyanide of potassium, whereby the cyanide of mercury is dissolved, and the carbonate of lead containing alkali remains undissolved.

From a mixture of the protoxide of mercury, cinnabar and minium, the first, along with a part of the oxide of lead, may be removed by means of nitric acid, (and the oxide of lead in this solution can be first thrown down by dilute sulphuric acid, and then the mercury by sulphydric acid or the chloride of tin); the lead is removed from the residue, composed of cinnabar and the binoxide of lead, by heating it along with dilute chlorhydric acid, or by nitric acid, on the addition of a little oxalic acid; the cinnabar remains undissolved.

4. Oxides of Bismuth.

Teroxide, BiO_3; *Bismuthic acid,* BiO_5.—Bismuth is found native, and as the teroxide and tersulphide (Bismuth-glance). Nitric acid is the best solvent for the metal and all its compounds.

Teroxide of bismuth is formed by strong ignition of the metal in the air, or by heating the nitrate. It is a lemon-yellow powder, becoming darker every time it is heated; not soluble in water. Its salts are colorless; their solutions, if there is not too much free acid present, are decomposed by water, and the white basic salt is precipitated.* The acid which has been set free always holds some of the teroxide in solution. The decomposition of the chloride is more complete, on which account, in examining for small quantities of bismuth, the solution in chlorhydric acid is evaporated to a few drops, and these are then thrown into water. The precipitated white powder is insoluble in tartaric acid, or the tartrate of potassa, which distinguishes it from the oxide of antimony.

Sulphydric acid, and *sulphide of ammonium* throw down the brown tersulphide of bismuth ($Bi S_3$), insoluble in excess of sulphide of ammonium.

Ammonia and *caustic potassa* throw down the white hydrated oxide, insoluble in excess of the reagents, though becoming yellow when boiled with the latter.

Alkaline carbonates throw down the white carbonate ($Bi O_3, C O_2$), only slightly soluble in excess of the precipitant.

Chromate of potassa throws down the yellow chromate, soluble in nitric acid, and insoluble in potassa. *Iodide of potassium* gives a brown, *ferrocyanide of potassium* a white, and *ferricyanide of potassium* a bright yellow precipitate.

Zinc, and some other metals precipitate metallic bismuth in a spongy form.

Besides *bismuthic acid* ($Bi O_5$), there exists some intermediate oxides, which can be considered as compounds of the acid with the teroxide. They are brown or dark-red powders, which yield the teroxide on ignition, and with chlorhydric acid evolve chlorine.

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* E. g. $3 Bi Cl_3 + 6 H O = (Bi Cl_3, 2 Bi O_3) + 6 H Cl$: or $Bi O_3, 3 N O_5, 9 H O = (Bi O_3, N O_5, 2 H O) + (2 N O_5, 7 H O)$.

All the compounds of bismuth, when heated along with soda on charcoal, afford brittle metallic grains, and a yellow incrustation.

Bismuth is most certainly recognized by the precipitation of its salts (especially the terchloride) on the addition of water; the precipitated basic salt is insoluble in tartaric acid, potassa, and in sulphide of ammonium. The teroxide may be distinguished from the oxide of lead by its insolubility in potassa, and by the precipitate produced in the oxide of lead by sulphuric acid. This acid serves, on this account, for the complete separation of the two metals when in the nitric acid solution; the best precipitant of the teroxide of bismuth is carbonate of ammonia at the boiling point; after the ignition of the precipitate, the teroxide remains. Tersulphide of bismuth is distinguished from sulphide of mercury by its solubility in nitric acid.

5. Oxides of Copper.

Suboxide, Cu_2O, and *Protoxide*, CuO. — Copper is found native, as suboxide (Red copper ore), as carbonate (Malachite and Azurite), as sulphide (Copper-Glance) and in union with other sulphides in Copper-pyrites, Bournonite, Gray copper ore, etc. Nitric acid is the best solvent of the metal or its compounds; the solution always contains the protoxide.

a. *Suboxide of copper*, when anhydrous, is a red powder, and of an orange-yellow color when in the state of a hydrate. It is produced by igniting the protoxide along with the metal, or by boiling the salts of the protoxide with sugar, arsenious acid, etc., in the presence of an excess of alkali. Along with sulphuric acid, it is resolved into metallic copper and a protosalt; with chlorhydric acid into the white subchloride of copper (Cu_2Cl), which is slightly dissolved by water, and more easily by chlorhydric acid. Its almost colorless solutions in acids and in ammonia, on exposure to the air, quickly become the blue or green compounds of the protoxide.

b. *Protoxide of copper* is a black powder when anhydrous, in the state of a hydrate a greenish blue, insoluble in water and soluble in almost all the acids. Its anhydrous salts are almost white,—those which are hydrates are green or blue.

Sulphydric acid, and *sulphide of ammonium* precipitate the black sulphide of copper (CuS) which readily oxidizes on exposure to the air, insoluble in chlorhydric acid and in sulphide of potassium, soluble in cyanide of potassium, and only very slightly soluble in sulphide of ammonium.

Caustic potassa, when cold, throws down the greenish-blue hydrated oxide ($CuO, 2HO$), and at boiling heat the black oxide (CuO); *ammonia* throws down at first a greenish basic salt, then the blue hydrate, which is soluble in excess of the reagent, giving a beautiful azure blue, which color is perceptible in moderately thin layers, even though it has been diluted with 100,000 times its quantity of fluid.

Carbonate of ammonia acts in a similar way.

Cyanide of potassium throws down the yellowish-green cyanide of copper ($CuCy$), soluble in excess of precipitant. *Iodide of potassium* throws down all the copper as the white subiodide (Cu_2I) (in the presence of sulphurous acid or the protosalts of iron); *ferrocyanide of potassium* precipitates, even in very dilute solutions, the brownish-red ferrocyanide of copper ($Cfy, 2Cu, 7HO$), insoluble in chlorhydric acid, soluble in ammonia, decomposed by potassa with the separation of the hydrated oxide of copper.

Polished metallic iron, in contact with a solution of the protoxide of copper not too acid, becomes covered with a copper-red coating of the latter metal; zinc precipitates metallic copper of a black color.

Borax and *phosphate of ammonio-soda*, with the compounds of the protoxide, afford beautiful green pearls, which become brownish red in the reduction flame (on the addition of tin). Treated with soda and cyanide of potassium on charcoal, the compounds of copper give copper-red metallic spangles, of which the smallest trace may be discovered, if the fused mass is washed with water in an agate mortar.

The solubility of the protoxide of copper in ammonia, and the deep blue color thus produced, its behavior towards ferrocyanide of potassium in acid solutions, and towards soda and cyanide of potassium, when heated on charcoal, allow copper to be detected easily.

Copper, in acid solution, can be separated from the metallic oxides of the foregoing groups, by means of sulphydric acid. The sulphide should be washed with sulphydric acid water. Silver is separated from copper by chlorhydric acid; lead by sulphuric acid; bismuth by carbonate of ammonia, or by cyanide of potassium, in which the oxide of bismuth is insoluble; mercury by treating the sulphides with nitric acid, or more completely by igniting them by themselves, or in chlorine gas.

6. [OXIDE OF CADMIUM. CdO.]

Cadmium is mostly found in company with zinc; it is more volatile than the latter; when heated in the air it readily burns, forming the oxide; is soluble in chlorhydric and sulphuric acid, with the disengagement of hydrogen gas, and more readily soluble in nitric acid. The oxide is a brown infusible powder, whose hydrate is white, and whose salts are colorless, most of them soluble in water, and all of them soluble in chlorhydric acid.

Sulphydric acid throws down, even in strong acid solutions, the sulphide of cadmium (CdS) at first lemon-yellow, but afterwards orange-yellow, which is insoluble in sulphide of ammonium, in caustic alkalies, and in cyanide of potassium.

Caustic potassa throws down the white hydrated oxide, insoluble in excess; *ammonia* produces the same precipitate, which is redissolved in excess of the precipitant, and from this solution, sulphydric acid precipitates the sulphide.

Alkaline carbonates, also *carbonate of ammonia,* throw down the white carbonate (CdO, CO_2) which is insoluble in excess of the precipitant.

Alkaline phosphates and *oxalates* give white precipitates, insoluble in water, though soluble in ammonia.

Ferrocyanide of potassium gives a white, and *ferricyanide of potassium* a yellow precipitate,—both are soluble in chlorhydric acid; the *cyanide of cadmium* is soluble in cyanide of potassium, from which sulphydric acid precipitates the sulphide.

Zinc throws down the metal as a dendrite (in an arborescent form). All the compounds of cadmium, when heated on charcoal along with soda and cyanide of potassium, give a brownish-red incrustation.

The oxide of cadmium, in acid solution, is separated from the metallic oxides of the former groups by sulphydric acid; it is distinguished from the protoxide of copper (independent of the color of its salts) by the insolubility of its carbonate in excess of carbonate of ammonia, and of its sulphide in cyanide of potassium; from the oxides of lead, bismuth, and mercury, by its solubility in ammonia; from the oxides of lead and silver, moreover, because its salts are not precipitated by sulphuric or chlorhydric acid, and from the oxide of bismuth, since it is not precipitated by the addition of water. Its sulphide is distinguished from the sulphide of mercury by its solubility in concentrated chlorhydric acid and nitric.

For the determination of cadmium in zinc ore, the latter is digested with aqua-regia, the solution diluted with water is then saturated with sulphydric acid, the precipitate being washed with sulphydric acid water is dissolved in nitric acid, precipitated by the addition of carbonate of ammonia, and gently digested. If the oxides of lead and bismuth are absent, the precipitate consists only of the carbonate of cadmium; the supernatant liquid contains the protoxide of copper.

7. [Oxide of Palladium. PdO.]

Palladium is the companion of platinum ores, and Brazilian gold dust. It is soluble in nitric acid and aqua-regia, giving a reddish-brown color; the solution contains the oxide. Its salts, on ignition, yield the metal.

Sulphydric acid and *sulphide of ammonium* throw down the dark-brown sulphide of palladium (PdS), insoluble in sulphide of ammonium, soluble in strong acids.

Iodhydric acid, and *iodide of potassium* precipitate the black *iodide of palladium* (PdI), which is only formed after some time when the solution is dilute. (This precipitate serves for the detection of iodine in mineral springs).

Cyanide of potassium (and also the cyanide of mercury) throw down the yellowish-white cyanide of palladium (Pd Cy), soluble in cyanide of potassium, and in much chlorhydric acid.

Caustic potassa gives a brown precipitate which is soluble in excess of the precipitant; but *ammonia* gives a precipitate, only in a concentrated solution of the chloride of palladium, soluble in excess of ammonia; from the ammoniacal solution, chlorhydric acid precipitates most of the palladium as a lemon-yellow chloride of palladium.

Chloride of ammonium does not precipitate the protosalts of palladium. Zinc, iron, sulphurous acid, protosulphate of iron, and the formates reduce the metal from the salts of palladium.

Chloride of tin and chlorhydric acid produce, even in dilute solutions, a green color.

Palladium remains in the mother liquid, after the precipitation of platinum by chloride of potassium, or of ammonium, from a solution of platinum ore in aqua-regia. This mother liquid is deprived of the metals it contains, through precipitation by means of iron or zinc; the precipitate is dissolved again in aqua-regia, and evaporated to drive off excess of acid, the palladium is then precipitated from the solution, after it has been made as neutral as possible, by cyanide of mercury. The same process is adopted with gold dust containing palladium.

8. [SESQUIOXIDE OF RHODIUM. R_2O_3.]

Rhodium is contained in platinum ores to the amount of 0.4 to 1.0 per cent. It is soluble in acids only when in an alloyed condition; it is soluble on fusion with bisulphate of potassa: it is oxidized at a red heat when mixed with potassa and nitre. Solutions of the sesquioxide of rhodium are of a rose-red color; they are with difficulty thrown down by *sulphydric acid*, as a brown sulphide of the metal, which is insoluble in sulphide of ammonium; the supernatant liquid remains of a rose red. Iron and zinc throw down the metal in a black pulverulent form.

Rhodium is found (after the precipitation of palladium by cyanide of mercury, as described above) by evaporating the decanted liquid, along with chloride of sodium and chlorhydric acid, to dryness, then treating the residue with alcohol, when the chloride of rhodium-sodium is left behind, which can be reduced by being heated in hydrogen gas.

9. [OXIDES OF OSMIUM.]

Osmium is found, in platinum ores, alloyed with iridium; *osmious acid* OsO_3, and osmic acid, OsO_5, are the most important of its oxygen-compounds. Osmious acid exists only in combination with bases; osmic acid is colorless, very fusible and volatile, diffusing poisonous vapors, resembling the odor of chlorine, which greatly irritate the eyes; they arise on heating the metal, or its lower oxides, with free access of oxygen. Its solutions color the skin black, and are readily reduced by sulphurous acid, formic acid, and many of the metals, the osmium being separated in a metallic condition. Sulphide of osmium is a blackish brown, insoluble in sulphide of ammonium.

For the separation of osmium from iridium in the platinum-residue, see iridium.

II. METALLIC OXIDES OF THE SECOND SECTION OF THE FIFTH GROUP.

1. Oxides of Antimony.

Teroxide of antimony, SbO_3, and *antimonic acid*, SbO_5. — Antimony is mostly found as the tersulphide (Gray Antimony) in union with other sulphides (FeS, PbS, Cu_2S, AsS_3). It is brittle, perfectly volatile before the blowpipe flame, producing white inodorous fumes of the oxide. It is readily soluble in chlorhydric acid, with the addition of a little nitric acid; with nitric acid alone, it is converted into the teroxide of antimony and antimonic acid, both of which are insoluble in excess of nitric acid, but soluble in tartaric acid; when its compounds are fused along with nitre, antimonic acid alone is produced.

All the sulphur compounds of antimony are soluble in hot concentrated chlorhydric acid, being converted into the terchloride, $SbCl_3$, and sulphydric acid is evolved; in the higher sulphides, there is also a separation of sulphur.

a. *Teroxide of antimony* is a white fusible powder, which is volatile at a red heat; its salts, not being very persistent, are decomposed by water and a white basic salt is separated (ex. gr. $5SbCl_3 + 15HO = (SbCl_3, 5SbO_3) + 15HCl$). Tartaric acid prevents this decomposition.

Sulphydric acid throws down, in solutions of the teroxide of antimony, the orange-red tersulphide (SbS_3), which is soluble in sulphide of ammonium and potassa, only slightly soluble in ammonia, and insoluble in bicarbonate of ammonia. A dilute solution of tartar emetic, free from acid, is colored orange-red by sulphydric acid; on the addition of an acid, the sulphide is precipitated.

Ammonia, and *the alkaline carbonates* throw down white, bulky precipitates of the teroxide, insoluble, or only slightly soluble in excess of the precipitant, (tartaric acid prevents this precipitation); the teroxide of antimony is soluble in caustic potassa.

Chloride of gold and *nitrate of silver* give black precipitates in an alkaline solution of the teroxide of antimony; that produced by the silver is *insoluble* in ammonia, which serves to distinguish the teroxide of antimony from antimonic acid.

Oxalic acid gradually precipitates *all* the teroxide in a chlorhydric acid solution of the teroxide of antimony; tartaric acid prevents the precipitation.

Chloride of gold throws down only metallic gold, in a solution containing much free chlorhydric acid (determination of $Sb\,O_3$ when in combination with $Sb\,O_5$).

Metallic zinc, also iron and tin precipitate from the terchloride of antimony the metallic antimony as a black powder; and which, moreover, along with free chlorhydric acid (in Marsh's apparatus) evolves the inodorous antimonietted hydrogen gas ($Sb\,H_3$). If this gas be conducted through a glass tube heated to a red heat, a shining ring of metallic antimony is deposited in the cold portion of the tube, which on being heated still more intensely in a stream of hydrogen, before it volatilizes, *melts* into little shining globules, recognizable by the microscope, and develops *no alliaceous odor.*. If a a porcelain tile is held in the flame of the gas streaming out, spots are formed on it which are blacker and less lustrous than those of arsenic; and which are not altered on dropping on them a concentrated and alkaline solution of the hypochlorite of soda. They are converted into the white oxide by nitric acid, and are completely soluble in a mixture of a drop of nitric acid, and a drop of chlorhydric, which solution when carefully freed from excess of acid by evaporation, gives a fiery-red precipitate with sulphydric acid water. If moistened with sulphide of ammonium, and gently evaporated, they become orange. If sulphydric acid gas be passed through the heated glass tube, containing an antimony-mirror, then the mirror is converted into the *black* or partially *orange-red* sulphide,* which is volatilized as terchloride of antimony and sulphydric acid, by passing chlorhydric acid gas over it.

b. *Antimonic acid* is a lemon-yellow infusible powder, passing over into the state of antimonious acid, the antimoniate of the oxide of antimony $(2\,Sb\,O_4 \quad Sb\,O_3, Sb\,O_5)$, with the disengagement of oxygen, on being exposed to a red heat; as a hydrate, it is white. There are two modifications of antimonic acid which are very similar, and on this account, difficult to distinguish; one is formed as a hydrate $(Sb\,O_5, 5\,H\,O)$, by heating antimony along with nitre or nitric acid; it is quite insoluble in water and in ammonia, though slowly soluble in chlorhydric or tartaric acid; the other (meta-antimonic acid) is formed by the precipitation of the perchloride of antimony by water, or by heating an alkaline antimoniate with a great excess of caustic alkali; its hydrate $(Sb\,O_5, 4\,H\,O)$ is by degrees soluble in ammonia, and in much cold water, from which solutions, however, it can be precipitated by acids. The potassa-salt of the latter $(2\,K\,O, Sb\,O_5)$ serves as a reagent for soda; when dissolved in water it gradually becomes the common antimoniate of potassa $(K\,O, Sb\,O_5)$, which does not precipitate the salts of soda, and is made turbid by chloride of ammonium.

A chlorhydric acid solution of antimonic acid gives no

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* Amorphous tersulphide? — TRANS.

precipitate with *terchloride of gold* and *oxalic acid;* an alkaline solution gives, with nitrate of silver, a yellowish-white precipitate of the antimoniate of silver, which is completely soluble in ammonia.

On the insolubility of the antimoniate of soda rests one of the best methods for the separation of antimony from other metals, and particularly from arsenic. Any compound of antimony (ex. gr. the sulphide) being intimately mixed in a porcelain crucible with four parts of nitrate of soda, and two parts of anhydrous carbonate of soda, and heated until the mass becomes entirely white, then treated when cold, with water (or still better, with very dilute alcohol), *all* the antimony remains as the antimoniate of soda (NaO, SbO_5), the arsenic, as an arseniate of the alkali, is found in the solution.

Antimony, in an acid solution, is separated from the metallic oxides of the preceding groups by sulphydric acid; from the metals of the first section of the fifth group by digesting the sulphur-compounds (or even the oxides) with yellow sulphide of potassium, or of ammonium, and then precipitating the sulphide of antimony from the filtrate by means of a dilute acid. Compounds of sulphide of antimony along with basic metallic sulphides, as Zinkenite (PbS, SbS_3); and Bournonite ($3Cu_2S, SbS_3 + 6PbS, 2SbS_3$), may be oxidized with nitric acid, saturated with potassa, and digested with the yellow sulphide of potassium; or the compound is melted along with three parts of dry carbonate of soda, and two parts of sulphur in a covered porcelain crucible, and the mass when cold treated with hot water, when the sulphides of lead and copper are left behind. Ruby-silver-ore ($3AgS, SbS_3$) is decomposed by being heated in chlorine gas, when the antimony and the sulphur are volatilized as chlorides, and the chloride of silver remains. *Gray antimony* (commercial tersulphide of antimony), when finely pulverized, is soluble in fuming chlorhydric acid, more readily so in aqua-regia, if only a small quantity of nitric acid has been taken.

All the compounds of antimony (excepting the sulphate), when fused along with cyanide of potassium or soda on charcoal, yield *brittle* metallic grains, which are entirely volatile before the blowpipe (possessing the odor of garlic only when arsenic is present); at the same time a white incrustation of the oxide will be formed which is easily volatilized by heat. The oxides or sulphides of antimony which are united with an alkaline base, are completely volatilized by repeated ignition along with chloride of ammonium, whilst an alkaline chloride of antimony remains.

2. Oxides of Tin.

The protoxide of tin, $Sn O$, and *the Binoxide* (*Stannic acid*), $Sn O_2$. — Tin is mostly found as the oxide (Tin-ore). It is soluble in hot chlorhydric acid, with the evolution of hydrogen, being converted into the chloride ($Sn Cl$); its solution in aqua-regia contains ($Sn Cl_2$). It is converted by nitric acid into the peroxide of tin, which is insoluble in excess of acid; the metal also forms the oxide, on ignition in the air.

a. *The protosalts of Tin* (the most common is the protochloride) are colorless; those which are neutral are rendered turbid by water, they absorb oxygen from the air, and if there is not sufficient free acid present, the white oxide separates.

Sulphydric acid and *sulphide of ammonium* throw down the dark-brown sulphide ($Sn S$), which is insoluble in yellow sulphide of ammonium or sulphide of potassium, so far as it is converted by them into the bisulphide of tin (SnS_2); acids give a yellow precipitate in this solution.

Ammonia and *Carbonates of alkalies* throw down the white hydrated oxide, not soluble in excess of precipitant; *potassa-lye* redissolves the hydrate.

Protochloride of tin is one of the most powerful reducing agents; it changes the salts of the sesquioxide of iron and protoxide of copper into those of the protoxide of iron and suboxide of copper; it precipitates the pure metal from the salts of many heavy metals (gold with a purple red color; the white subchloride of mercury from the chloride, there being an excess of the latter, or in an excess of the protochloride of tin (heat being used) the metallic mercury will be obtained). On heating with sulphurous acid there is produced the yellow bisulphide of tin mixed with the binoxide of tin ($6SnO + 2SO_2 \quad 5SnO_2 + SnS_2$).

b. *Binoxide of Tin*, or *Stannic acid* is a white powder, becoming yellow every time it is heated, quite insoluble in water, and, after ignition, in acids, especially nitric acid; it exists, like antimonic acid, in two modifications. The one (the binoxide a) is completely precipitated as a hydrate (SnO_2, HO) from the bichloride of tin by *Ammonia;* it is soluble in chlorhydric acid,—the solution is not precipitated by acid, and tartaric acid prevents its precipitation by ammonia. *Carbonate of potassa* throws down a bulky precipitate of the oxide, soluble in excess; *Tincture of galls* occasions no precipitate.

The other modification (the binoxide b, or metastannic acid) is produced by the action of nitric acid on metallic tin; its hydrate ($SnO_2, 2HO$) is soluble in chlorhydric acid after they have been heated together, and on the addition of water. The chlorhydric acid solution is precipitated by sulphuric acid; tartaric acid does not prevent a precipitation by ammonia. *Carbonate of potassa* gives a precipitate of the binoxide, insoluble in excess. *Tincture of galls,* after some time, occasions a whitish-yellow precipitate.

Both these modifications are completely thrown down from their *dilute* chlorhydric acid solutions, by boiling, especially in the presence of an alkaline sulphate; the smaller the quantity of free acid present, the more rapid will be the precipitation; both are completely soluble in caustic potassa or soda, and both are precipitated from an acid solution, especially on being warmed, *by sulphydric acid* as the yellow bisulphide of tin ($Sn\,S_2$), which is very soluble in sulphide of ammonium, and somewhat more difficultly soluble in caustic alkalies, and is converted into the binoxide on being ignited in the air.

All the compounds of tin, when heated on charcoal along with soda and cyanide of potassium, yield a ductile metallic grain, without any incrustation.

Tin, in acid solution, is separated from the metallic oxides of the preceding groups, by sulphydric acid; from lead, silver, mercury, copper, cadmium, and bismuth, by digesting the sulphides (or even the oxides) with sulphide of ammonium, or (in alloys) with concentrated nitric acid, when the binoxide (b) is left behind; insoluble in excess of nitric acid; — the solution contains the nitrates of the other metals; from copper and lead, also, by heating in dry chlorine gas, when the bichloride of tin distils off. Tin is recognized, when antimony is present, since both are converted by nitric acid into oxides, through the oxidation of their alloys or sulphides, and if these, after being washed, are boiled with tartaric acid, the binoxide of tin will be left back, which yields, on being heated along with soda and cyanide of potassium, a *ductile* metallic globule; or both are reduced to a metallic globule by fusion along with cyanide of potassium, and this is then fused by itself for some time on charcoal in the reduction flame, when the antimony volatilizes accompanied with the formation of a white incrustation, while the tin remains. If this metallic globule is boiled along with chlorhydric acid, and a solution of corrosive sublimate be added, a white precipitate of calomel is produced. For their more complete (quantitative) separation, the metals (or their sulphides) are first oxidized with strong nitric acid, and the oxides then fused in a silver crucible with excess of caustic soda, when, on treatment with water, (or still better with dilute alcohol,) the antimoniate of soda remains undissolved, while the soda-binoxide of tin (Zinnoxydnatron) is taken up in solution and can be removed by filtration. The presence of the protoxide of tin, in combination with the binoxide, can be recognized by its comportment with the terchloride of gold and the chloride of mercury, as well as by the brown color of the precipitate produced by sulphydric acid. For the separation of tin and antimony from arsenic, see the last.

3. Oxides of Arsenic.

Arsenious acid, AsO_3, and *Arsenic acid,* AsO_5. — Arsenic is found native as a sulphide, as an arsenide (in combination with iron, nickel and cobalt), and as an arseniate; in traces it is widely spread as an almost constant companion of sulphur, iron, copper, tin, and antimony; it is also a constituent of the waters of many mineral springs, — for its detection in which, the ochrous deposits of the same are selected.

Metallic arsenic is volatile; when heated in the air, it burns forming arsenious acid, diffusing a penetrating alliaceous odor; in moist atmosphere it is gradually resolved into a brown powder, from which either water or chlorhydric acid extracts arsenious acid. The metal is not acted on by chlorhydric acid; nitric acid, when very concentrated, converts it into arsenic acid, but otherwise always into arsenious acid; chlorine (also aqua-regia, chlorate of potassa, and chlorhydric acid, etc.) produces with all the compounds of arsenic, without exception, arsenic acid; the same effect is also produced on fusion along with a nitrate.

a. *Arsenious Acid* is either an amorphous, porcelain-like, crystalline mass, or a white granular powder. It is with difficulty soluble in cold water (requiring about fifty parts), more easily so in that which is boiling (in 10–12 parts), and still more soluble in chlorhydric acid and in alkalies. Its vapor is perfectly inodorous, the alliaceous odor only being recognized when arsenious acid is volatilized on charcoal, or on any support which exercises a reduction-power.

Its aqueous solution is only colored yellow by *sulphydric acid*, but in the presence of chlorhydric acid it is immediately and completely precipitated as the yellow tersulphide of arsenic (AsS_3); this is very soluble in ammonia and carbonate of ammonia, in sulphide of potassium or sulphide of ammonium, in the fixed caustic and carbonated alkalies ($2\,AsS_3 + 5\,KO = AsO_3, 2\,KO + AsS_3, 3\,KS$), and also in nitric acid; it is insoluble in chlorhydric acid. It is again completely precipitated from its solution in alkalies or sulphide of ammonium, as the tersulphide of arsenic, by means of chlorhydric or nitric acid.

An aqueous solution of arsenious acid gives with the *nitrate of ammonia-silver* a yellow precipitate ($2\,AgO$,

AsO_3), with the *ammonio-sulphate of copper*, a yellowish green ($2\,CuO, AsO_3$), and with excess of *lime-water*, a white ($2\,CaO, AsO_3$). All these precipitates are very soluble in ammonia, and in chloride of ammonium, as well as in nitric acid.

The chlorhydric acid solution of arsenious acid furnishes a precipitate of metallic gold, when the *chloride of gold* is added; from the weight of the latter the arsenious acid may be computed ($3\,AsO_3 + 2\,AuCl_3 + 6\,HO = 3\,AsO_5 + 2\,Au + 6\,HCl$).

In a mixture of chloride of ammonium, ammonia and sulphate of magnesia, arsenious acid cannot be precipitated.

Chromate of potassa takes a green tinge with arsenious acid, and the *permanganate of potassa* a brownish yellow, with the formation of arsenic acid.

If a solution of arsenious acid in caustic alkali be warmed with a *little* protosulphate of copper, there will be a precipitate of the red suboxide of copper ($AsO_3 + 4\,CuO = AsO_5 + 2\,Cu_2O$). Arsenious acid, dissolved in chlorhydric acid, will deposit a grayish metallic crust on polished metallic copper.

Along with zinc and sulphuric or chlorhydric acid, in *Marsh's* apparatus, arsenious acid (and also arsenic acid) develops arsenietted hydrogen gas (AsH_3), which has a very offensive odor, and, being ignited, burns with a bluish-white flame, forming arsenious acid and water. If a piece of cold porcelain (not the imitation porcelain which contains lead, stone ware, nor fayence) be held in this flame, there will be deposited (though there be only traces of arsenious acid present) brown, steel-gray, or almost black shining spots of metallic arsenic, which disappear immediately on the addition of a few drops of a concentrated alkaline solution of the hypochlorite of soda, and which also form a clear solution, in a drop of hot nitric acid, containing arsenious or arsenic acid. If there be added to this nitric acid solution a drop of solution of nitrate of silver, and then a rod moistened with ammonia be held close over the spot without shaking it, the drop colors itself yellow, on account of the formation of arsenite of silver, or brownish-red from arseniate of silver. Spots of antimony will not show these reactions.

If a dried glass tube, about one line in diameter, perfectly free from lead, of difficult fusibility, and drawn out to a capillary termination at one end, be taken, and the gas being carefully dried by chloride of calcium be now passed through this tube, having previously heated the middle part to a red heat, there will be, beyond the heated portion of the tube, a dark stain of metallic arsenic, at first brown, and afterwards mirror-like, which gradually becomes opaque with large quantities of the metal. This mirror is volatilized on being heated in a current of hydrogen (more readily so than that of antimony), without previously fusing into little globules, and the gas which streams forth has a decided alliaceous odor. If the arsenical mirror be warmed, while sulphydric acid gas is passed over it, it is converted into the very volatile *yellow* sulphide of arsenic, which is not decomposed by chlorhydric acid gas.

Arsenietted hydrogen, being passed through hot concentrated nitric acid, yields the soluble arsenic acid; antimonietted hydrogen, under similar circumstances, yields a white precipitate of antimonic acid, which remains undissolved, even after the full evaporation of the free nitric acid and treatment with hot water; the aqueous solution shows the reactions of arsenic acid; by passing arsenietted and antimonietted hydrogen gas through a solution of the nitrate of silver, all the antimony is precipitated as an antimonide of silver (Ag_3Sb), whilst all the arsenic remains in solution as arsenious acid, and, by neutralization with ammonia, it can be precipitated as the yellow arsenite of silver.

The vapor of arsenious acid is easily reduced by ignited charcoal, and the metallic arsenic is separated ($AsO_3 + 3C = As + 3CO$). If a small quantity of arsenious acid be placed in the end of a very narrow tube, and a splinter of freshly prepared charcoal, about half an inch long, be placed over it, and the part of the tube containing the charcoal being held horizontally in the flame of a spirit lamp be heated with care so that the arsenious acid is only brought into the flame when the charcoal is ignited, then there will be deposited above the latter a dark ring, with metallic lustre, which may be driven up and down the upper portion of the tube by the application of heat, changing eventually into colorless, shining and volatile crystals of arsenious acid.

When arsenious acid is heated along with cyanide of potassium, there is formed the cyanate of potassa and all the arsenic is volatilized, ($2AsO_3 + 3CyK = 2As + 3[CyO, KO]$). If, in a tube closed at one end by fusion, a small portion of arsenious acid is heated with a piece of dry acetate of potassa of the size of a pin's head, the peculiar, exceedingly offensive odor of the oxide of Kakodyl will be developed ($2C_4H_3O_3 + AsO_3 = C_4H_6OAs + 4CO_2$).

If arsenious acid, or any other arsenical compound, mixed with a large quantity of organic substances, be heated in a distilling apparatus along with chloride of sodium and excess of concentrated sulphuric acid, the chloride of arsenic will be distilled over, and can be easily detected as arsenious acid in the watery distillate.

If tersulphide of arsenic be heated along with cyanide of potassium (or still better, with twelve parts of a perfectly dry powder, composed of one part of cyanide of potassium and three of carbonate of soda), then will all the arsenic be separated in metallic form, while the sulphur remains behind as a sulphcyanide ($2\,AsS_3 + 3\,KCy = 2\,As + 3\,CyKS_2$). This experiment, which will recognize a very small quantity of arsenic if some care be taken, is best performed in this way; — the dry mixture of sulphide of arsenic, soda and cyanide of potassium is deposited, by means of a piece of stiff paper bent in the form of a gutter, in a glass tube, eight or nine inches long, and from four to five lines wide, — the tube having been drawn out at one end to a fine capillary bore for several inches. The tube thus prepared, is connected with an apparatus which furnishes a slow stream of carbonic acid (made from marble and chlorhydric acid) dried by passing through sulphuric acid. The place in the tube, where the mixture lies, should be gently warmed by a small spirit lamp until all moisture is driven away; then the tube is heated to redness between the mixture and its capillary extremity, and finally the mixture is heated by a second and larger spirit lamp, when an arsenical ring will be deposited near the beginning of the pointed extremity. It is essentially necessary here that all the moisture should be removed from the mixture, before its fusion, and the stream of carbonic acid be but a slow one. Under these circumstances, tersulphide of antimony will yield no metallic ring.

b. *Arsenic Acid* is a white, opaque mass, vitreous in appearance when freshly prepared; it is volatilized at a red heat as arsenious acid and oxygen gas; in the air it slowly deliquesces and is soluble in six parts of cold, or in two parts of hot water. Its solutions have a strong acid reaction. The arseniates are mostly colorless, and isomorphous with the phosphates; those which are insoluble in water are soluble in chlorhydric or nitric acid.

In solutions of the arseniates, made acid by chlorhydric acid at ordinary temperatures, *sulphydric acid* produces precipitates quite slowly (completely only after twenty-four hours), but on being heated up to 60° or 70° C. the precipitation is immediately effected. The precipitate is the pentasulphide of arsenic (AsS_5), which comports itself with solvents and reducing agents exactly as the tersulphide (AsS_3).

If a solution of an arseniate mixed with chlorhydric acid be heated along with sulphurous acid until the disappearance of the odor of the latter, then sulphydric acid will produce at once a precipitate of the tersulphide (AsS_3) so far as the arsenic acid has been reduced to the condition of arsenious acid ($AsO_5 + 2\,SO_2 = AsO_3 + 2\,SO_3$). For the complete reduction, several hours' treatment with sulphurous acid is required.

Nitrate of Silver produces a brownish-red precipitate ($3\,AgO, AsO_5$) with the neutral arseniates; *sulphate of copper* a pale greenish blue ($2\,CuO, HO, AsO_5$), *lime water* a white, very soluble in nitric acid, as well as in ammonia salts.

The salts of the sesquioxide of iron and *uranium* give yellowish-white, and the *protosalts of lead* white precipitates, which comport themselves similar to the corresponding phosphates.

If arsenic acid or an arseniate (though in very small quantity) be warmed along with excess of *molybdate of ammonia* and free nitric acid, the solution will acquire a yellow color, and gradually afford a yellow precipitate (see also phosphoric acid).

The arseniates which are soluble in water mixed with ammonia and chloride of ammonium, give with *sulphate of magnesia* a crystalline precipitate of the arseniate of ammonia-magnesia ($2\ MgO,\ NH_4O,\ AsO_5 + 12\ HO$), which serves for the separation and discrimination of arsenic acid from arsenious acid, and also for the determination of arsenic.

When a solution of an arseniate, acidified by chlorhydric acid, is heated to the boiling point along with hyposulphite of soda, the pentasulphide of arsenic will be thrown down ($5\ (NaO,\ S_2O_2) + AsO_5 = 5\ (NaO,\ SO_3) + AsS_5$).

The arseniates always yield arseniетted hydrogen in *Marsh's* apparatus.

The detection of arsenic is one of the easiest problems in analytical chemistry. The volatility of all its compounds, the extreme ease with which they can be reduced, taken in connection with its peculiar odor, its complete precipitation from acid solutions by sulphydric acid, and the formation of arseniетted hydrogen from the contact of an oxygen compound of arsenic with zinc and sulphuric acid, constitute fixed points for its determination.

If an arsenical compound is heated on charcoal (either by itself or with soda and cyanide of potassium) in the inner flame of the blowpipe, the characteristic alliaceous odor will be produced, which enables us to recognize the smallest traces of arsenic.

Arsenic is separated from the metallic oxides of the foregoing groups, — whether it be present as arsenious or arsenic acid, — in its chlorhydric acid solution by means of sulphydric acid; from the oxides of the first section of the fifth group by treating the sulphides (or the oxides) with sulphide of ammonium or sulphide of potassium, when the sulphide of arsenic is taken into solution, from which it is completely precipitated by saturation with chlorhydric or dilute sulphuric acid. Arsenic is completely separated from all the metals whose sulphides are non-volatile, by heating the sulphides, or the oxides, in sulphydric acid gas.

Discrimination and separation of Arsenious acid from Arsenic acid. Arsenic acid is completely precipitated by a mixture of chloride of ammonium, ammonia, and a soluble salt of magnesia, while arsenious acid is not affected by it; in the presence of the latter the acid filtrate gives a yellow precipitate with sulphydric acid. Arsenious acid reduces the terchloride of gold, — an effect not produced by arsenic acid. Arsenic acid is recognized in those arseniates which are not soluble in water, though soluble in acids (in which on this account, the precipitation as the arseniate of ammonia-magnesia is not applicable), by the addition of acetate of soda and a *very small* quantity of the sesquichloride of iron to the solution, previously as far as possible neutralized by ammonia. The precipitates of the arseniate of ammonia-magnesia, and of the sesquioxide of iron, can be easily distinguished from the corresponding phosphates by their comportment before the blowpipe, or in *Marsh's* apparatus.

Arsenic from tin. — We recognize arsenic easily in metallic tin by means of *Marsh's* apparatus, in which it is heated in its granular condition along with concentrated chlorhydric acid (without the addition of zinc). The sulphide of arsenic is recognized when mixed with the sulphide of tin, by the alliaceous odor which is evolved on heating the mixture before the blowpipe on charcoal along with soda and the cyanide of potassium, — the metallic tin remains behind in ductile metallic grains, without any incrustation; or the sulphides may be dissolved in chlorhydric acid with the addition of chlorate of potassa, and then the solution, after the excess of chlorine has been driven off by heat, can be tested in *Marsh's* apparatus. The separation of arsenic from tin is secured perfectly, if their sulphides (or even their oxides) be heated in a stream of sulphydric acid, when the sulphide of arsenic is volatilized and may be caught again by passing it through ammonia, while the sulphide of tin remains behind, which is converted into the peroxide by roasting. The sulphide of arsenic which is dissolved in ammonia can be precipitated by chlorhydric acid and determined as the arseniate of ammonia-magnesia, after its solution in chlorhydric acid and chlorate of potassa.

Arsenic from Antimony.—The presence of arsenic can be very easily recognized in metallic antimony by the arsenical odor it gives before the blowpipe. The sulphide of antimony is reduced by soda and cyanide of potassium; in testing the commercial sulphides, the residue which is left after treating a large quantity of the fine powder with concentrated chlorhydric acid, is properly employed for the purpose. All the sulphide of arsenic can be removed by digesting the freshly precipitated sulphides along with carbonate of ammonia, while the sulphide of antimony remains undissolved. These two metals can also be distinguished from each other by means of *Marsh's* apparatus. An arsenical solution containing antimony at first gives only arsenical spots. Small quantities of antimony in arsenical spots do not prevent their solution in hypochlorite of soda. Compare pages 72 and 80. A complete, practicable qualitative and quantitative separation of the two, in the absence of tin, is attained in the following way. (This is a continuation of the process described under head of antimony.)

The sulphides (the alloys or the weighed oxides) are dissolved in aqua-regia, or still better, in chlorhydric acid, with the addition of chlorate of potassa, mixed with tartaric acid, then with ammonia in excess, and at last the arsenic acid completely precipitated by a soluble salt of magnesia. The precipitate is washed with dilute ammonia. The antimony is thrown down from the filtrate, by means of sulphydric acid, after it has been acidified with chlorhydric acid.

Arsenic from Antimony and Tin. — a. *Qualitative.* All the arsenic (along with a little of the tin) is extracted from the mixed freshly precipitated sulphides by digestion along with carbonate of ammonia, and the precipitated sulphide of arsenic, obtained from this solution by means of chlorhydric acid and some sulphydric acid water, is tested, by reduction along with cyanide of potassium in a stream of carbonic acid gas, or by making a solution of it in the smallest possible quantity of aqua-regia, and using it in *Marsh's* apparatus. The remaining sulphides insoluble in carbonate of ammonia, are dissolved in chlorhydric acid, with the addition of a little chlorate of potassa, and then introduced into a small *Marsh's* apparatus; the tin is thrown down in it as a black metallic powder, which can be freed from zinc by washing, dissolved in hot chlorhydric acid, and then recognized by the chloride of mercury or sulphydric acid; the antimony is identified by the spots, which it deposits on porcelain, being insoluble in hypochlorite of soda.

b. *Quantitative.* The compound is completely oxidized with nitric acid, evaporated to dryness, and the residue fused along with excess of hydrate of soda (about eight parts) and some nitrate of soda, in a silver crucible. The mass is then softened with a little water, some alcohol (about one third the volume) is added, and the undissolved antimoniate of soda is washed out with dilute alcohol which contains some carbonate of soda. Tin and arsenic are precipitated from the filtrate, after it has been made acid by chlorhydric acid, by means of sulphydric acid, and the sulphides are treated as has already been described (p. 87). Or the filtrate is saturated with nitric acid, evaporated to dryness and treated with water, when the arsenic acid (which can afterwards be precipitated as the arseniate of ammonia-magnesia) is dissolved out, leaving the binoxide of tin, which still contains some arsenic acid. By heating in sulphydric acid gas, they can be separated, like the sulphides.

Examination of arsenic in judicial cases. — In conducting a judicial investigation, the problem for the chemist is, to obtain the arsenic in substance as a metal, and produce it in Court, since it is only in this form endowed with such characteristic peculiarities, that it cannot be mistaken for any other substance.

Before the chemical investigation, the contents of the stomach and intestines, as also the substances ejected in vomiting, are to be examined in order to find whether any undissolved arsenious acid is mixed with them. This is done by a careful examination of the substances when spread out in porcelain bowls, or by diluting the same with water and floating off the lighter organic substances. If milk-white grains are found, possessed of the peculiarities of arsenious acid, (see page 79,) then the arsenic itself should be obtained by reduction with charcoal (see page 82,) or in *Marsh's* apparatus. If the arsenic is not perceptible in substance or separable by mechanical means (which is the more common state of the case), then the whole mass of organic material, of the contents of the stomach, the vomited matters, the food, the stomach, the intestines, etc., must be first decomposed and dissolved.* The pap-like masses being heated are perfectly saturated with washed chlorine gas, then heated nearly to the boiling point in order to drive off the excess of chlorine, and filtered through paper which contains no smalt. The stomach and intestines, and the other organic matters, being cut into fine pieces are dissolved in the smallest possible amount of potassa-lye in the heat, saturated with dilute sulphuric acid, and the coagulated mass treated with chlorine gas. Or a small quantity of chlorate of potassa (free from lead) is gradually added to the mass composed of the fine pieces stirred up to a pap with dilute chlorhydric acid, and warmed in a water bath, until the fluid has become a clear yellow and thin; then heated for a long time, filtered when cold, and the insoluble portion washed on the filter with hot water. The filtrate should then be concentrated, in a water bath, to about one pound. The fluid thus prepared is saturated with washed sulphydric acid gas, whilst it is heated from 60° to 70° C., in order to hasten the precipitation. After standing twenty-four hours in a close vessel, and after the necessary evaporation of excess of sulphydric acid at a gentle

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* It is taken for granted that a careful examination must be previously made of all the materials (the sulphuric, chlorhydric, and nitric acid, the zinc, nitre, chlorate of potassa, and hydrate of potassa) and also of the utensils used in these operations, for the possible existence of arsenic in them. This is done most judiciously in Marsh's apparatus. The chlorate of potassa prior to using this test is converted by fusion into chloride of potassium, the nitre and hydrate of potassa into the sulphate, by sulphuric acid. It is further to be understood that arsenic may be introduced into the bodies of the poisoned by medicinal agents (the preparations of antimony and phosphorus, and even the hydrated sesquioxide of iron itself).

warmth, the sulphide of arsenic, colored dirty brown on account of the organic material precipitated along with it, is placed on a filter, and, after being washed, is dissolved in the smallest possible quantity of potassa-lye. The potassa-solution is then completely desulphurized by the addition of freshly precipitated pure teroxide of bismuth, and by heating; the filtrate is saturated with dilute sulphuric acid, and introduced into *Marsh's* apparatus. Or the precipitate of the sulphide of arsenic, with the filter, is digested in a large porcelain crucible along with concentrated nitric acid (free from chlorine) until the paper has entirely disappeared, neutralized with carbonate of soda, evaporated to dryness, and the mass heated to fusion. If a sufficient excess of nitrate of soda is present, it first becomes brown, then black, and finally melts, without detonation, forming a colorless liquid.* The cold saline mass is now heated with concentrated sulphuric acid, until all the nitric acid is *completely* driven off, then dissolved in a little hot water and poured into a *Marsh's* apparatus. It is indispensable that this apparatus be provided with a funnel tube for pouring in the liquid to be tested; and before it is poured in, the apparatus must be filled with hydrogen, the hydrogen kept continuously evolving, and the not easily fusible tube, through which the gas streams, heated to redness in one place (about the middle). If after an hour's ignition of the glass tube, there is produced neither a mirror nor a stain, which possesses the specified peculiarities of arsenic, (p. 80,) then is the absence of arsenic proved.

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* If the fused mass be treated with water (instead of sulphuric acid) there will remain undissolved somewhat of antimony as the antimoniate of soda, or a portion of copper as the black oxide.

Or we may place the organic masses to be examined, mixed with an equal weight of fused chloride of sodium, in a tubulated retort, which stands in connection with a tubulated receiver, whose exit tube dips in water. By degrees, concentrated sulphuric acid is added through the funnel tube, until all the chloride of sodium is decomposed, and heat is applied, after the mixture ceases foaming, until it boils. After long distillation, the distillate contains all, or nearly all the arsenic, as arsenious acid, dissolved in chlorhydric acid. This fluid is then either introduced directly into *Marsh's* apparatus, or it is precipitated by sulphydric acid and the resulting sulphide treated as above.

If no arsenic is found in the stomach and intestines, and it is conjectured that it has been removed partly by emesis and evacuations, or partly absorbed and carried into the blood and those organs of the body which are rich in blood, then the liver, spleen, lungs, heart, and kidneys are to be treated exactly as described above. If the bladder contain any urine, it is first examined, being made weakly acid by chlorhydric acid, and then saturated with sulphydric acid.

4. Oxides of Gold.

Protoxide, AuO, and *Teroxide,* AuO_3.—Gold is only found native. Its best solvent in the metallic condition is aqua-regia; the solution contains the terchloride ($AuCl_3$) corresponding to the teroxide. Gold is but slowly soluble in nitric acid.

Sulphydric acid precipitates the black tersulphide of gold, AuS_3, from cold solutions of the terchloride, which is soluble in yellow sulphide of ammonium and in aqua-regia; insoluble in nitric acid.

Fixed caustic alkalies only imperfectly precipitate the terchloride of gold; *ammonia* effects the separation of the reddish-yellow fulminating gold, $AuO_3, 2NH_3$. Most of the common metals, and also mercury, silver, and platinum reduce the gold to its metallic condition from such solutions as are free from nitric acid; this is still more readily effected by the *protosalts of iron, arsenious acid,* and *terchloride of antimony* dissolved in chlorhydric acid, *sulphurous acid, potassa-lye* containing *sugar, oxalic acid,* and many other organic compounds.* The precipitate usually forms a brown or purple-red powder, which shows the lustre of gold on being rubbed with a hard substance.

Protochloride of tin, containing some of the bichloride, gives, even in very dilute solutions, a purple-red color and a precipitate of gold-purple (purple of cassius), which, when freshly precipitated, is soluble in ammonia, with a purple-red color, but is insoluble in chlorhydric acid.

The compounds of gold, when ignited with soda or borax on charcoal, yield yellow, shining ductile metallic grains.

The recognition of gold presents no difficulties. Its precipitation in metallic form, even in the presence of most of the other metallic oxides, by means of protosulphate of iron, oxalic acid, arsenious acid, etc., serves for its sure detection and determination. Ores containing but little gold (roasted auriferous pyrites) only require digestion with chlorine water (or solution of bleaching powder (chlorkalk) with some chlorhydric acid), and the gold is then separated from the evaporated

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* ($AuCl_3 + 6(FeO, SO_3) = Au + 2(Fe_2O_3, 3SO_3) + Fe_2Cl_3$.
$AuCl_3 + 3C_2O_3 + 3HO = Au + 6CO_2 + 3HCl$).

solution by means of arsenious acid. In treating silver coin with nitric acid, there remains behind sometimes a small portion of gold as a black powder; gold can also be separated from silver and copper by heating with concentrated sulphuric acid.

5. Oxides of Platinum.

Protoxide, PtO, and *Binoxide*, PtO_2.—Platinum is found native in platinum ore; auriferous silver coins contain about $\frac{1}{100000}$ of platinum, which remains undissolved along with the gold, and some of the silver, on treating them with concentrated sulphuric acid. Aqua-regia is the only solvent of platinum; the solution contains the chloride ($PtCl_2$) corresponding to the binoxide. It is a reddish brown, and gives, with *chloride of ammonium* and *chloride of potassium*, crystalline orange-yellow precipitates of the double chloride of platinum and ammonium (Platinsalmiak, *Ger.*) NH_4Cl, $PtCl_2$, or of the double chloride of potassium and platinum, KCl, $PtCl_2$, which are almost entirely insoluble in alcohol, on which account they serve for the separation of platinum from its solutions, as well as for the detection and determination of ammonia and potassa. (See pages 1 and 2.) The double chloride of platinum and ammonium leaves, on ignition, pure spungy platinum; the double chloride of platinum and potassium is so completely decomposed by being heated with oxalic acid or in a stream of hydrogen gas, that water dissolves the chloride of potassium and leaves the platinum behind.

Sulphydric acid slowly precipitates, from solutions of bichloride of platinum, the blackish-brown bisulphide PtS_2, which is soluble in sulphide of ammonium and in aqua-regia, though insoluble in nitric acid.

Protochloride of tin produces a dark brownish-red color.

The bichloride of platinum is resolved on being heated into the dark-brown protochloride, $Pt\,Cl$ (chlorine gas being disengaged), from a solution of which, in chlorhydric acid, ammonia precipitates the ammonio-chloride of platinum, $Pt\,Cl, NH_3$.

Platinum ores contain from 74 to 86 per cent. of the metal, with small quantities of palladium, rhodium, iridium, osmium, ruthenium, iron, copper, and sometimes also silver and lead. It is mixed with grains of iridosmium, gold, magnetic iron, titanate and chromate of iron, spinelle, etc. To obtain the platinum, these ores are first treated with chlorhydric acid, by which the iron is withdrawn, then for a long time with aqua-regia, which dissolves the platinum together with the gold, palladium, some iridium, etc. After the expulsion of excess of acid by evaporation the platinum is precipitated by means of the chloride of ammonium. Or the solution is mixed with excess of lime in the dark, by which all the metallic oxides, with the exception of platinum, are separated. The platinum is precipitated from the filtrate, to which chlorhydric acid has been added, by means of zinc, and is freed from the zinc by digestion in chlorhydric acid, after which it is dissolved in aqua-regia. That portion of platinum ores, which is insoluble in acids, is treated as described under the head of iridium.

6. [Oxides of Iridium.]

Binoxide of iridium, $Ir\,O_2$, is the most important of the four oxides of this constantly occurring metal in platinum ores. Iridium is only soluble in aqua-regia when it is alloyed with platinum. By igniting the metal with nitre, or with hydrate of potassa and chlorate of potassa, the black sesquioxide of iridium is produced, which dissolves with a blackish-red color in aqua-regia, becoming the bichloride, $Ir\,Cl_2$. The concentrated solution of the latter gives, with chloride of ammonium, a blackish-red precipitate of the double chloride of iridium and ammonium, $NH_4Cl, Ir\,Cl_2$; this is decolorized and converted into an oxysalt by the protosulphate of iron, oxalic acid, protochloride of tin and sulphydric acid; the last then slowly produces a brown precipitate. Nitrate of silver produces at first an indigo-blue precipitate which gradually loses its color.

Irid-osmium (or the portion of platinum ores which is insoluble in aqua-regia), in order to obtain the metals separate, is finely pulverized and heated along with an equal volume of decrepitated chloride of sodium, in a stream of moist chlorine gas, by which means the most of the osmium passes over as an acid into the receiver containing alcohol, while the double chloride of iridium and sodium remains, soluble in hot water. From the dark reddish-yellow solution, on the addition of strong nitric acid, the osmic acid is distilled, the most of the iridium is precipitated from the concentrated residue by means of chloride of ammonium; and the remaining solution being evaporated to dryness along with excess of carbonate of soda, slightly ignited and washed out with hot water, will leave the black sesquioxide of iridium behind, which can then be reduced by being gently heated in hydrogen gas, freed by water from soda, and by concentrated chlorhydric acid from iron. For the reduction of osmic acid, its solution is heated along with formic acid, or it is evaporated along with ammonia and chloride of ammonium, and the dry mass heated in a retort, when the osmium remains.

To obtain Ruthenium, the watery solution of the mass which has been ignited in chlorine gas is mixed with some ammonia and then heated, when the oxides of ruthenium, osmium, and iridium are separated. For the removal of the osmium as osmic acid, the mixture is distilled along with aqua-regia, evaporated to dryness, and ignited along with hydrate of potassa and nitre. On treating the residue with water, the rutheniate of potassa is dissolved out (which by exact neutralization with nitric acid is precipitated as the black oxide of ruthenium), whilst the sesquioxide of iridium is left behind.

Or the irid-osmium may be fused with a mixture of equal parts of hydrate of potassa and chlorate of potassa, and treated with water, when the sesquioxide of iridium remains behind, while the osmiate and rutheniate of potassa are taken up in the solution.

For testing the presence of rhodium in iridium, the latter is fused for some time with bisulphate of potassa, treated with water, and after being boiled with chlorhydric acid precipitated by potassa as a brownish-yellow hydrated sesquioxide of rhodium, which can be reduced to the metallic condition by ignition in hydrogen gas.

7. [OXIDES OF TUNGSTEN.]

Binoxide, $\mathrm{Wo\,O_2}$, and *Tungstic acid,* $\mathrm{Wo\,O_3}$. — Tungsten is found as tungstic acid in Wolfram $(\mathrm{Fe\,O, Mn\,O}), \mathrm{Wo\,O_3}$, and in the mineral Tungsten, $\mathrm{Ca\,O, Wo\,O_3}$. Tungstic acid when anhydrous, is a yellow powder quite insoluble in acids; when existing as a hydrate, it is white. Its compounds with alkalies are soluble in water, those with most of the other metallic oxides, insoluble. If tungstic acid is heated in hydrogen gas, or tungstate of potassa along with chloride of ammonium, the brown or black binoxide of tungsten, $\mathrm{Wo\,O_2}$, is produced, which is insoluble in acids; if the acid (or even a tungstate) be brought into contact with zinc and chlorhydric, sulphuric, phosphoric, or acetic acid, the blue tungstate of the binoxide of tungsten is produced.

If sulphide of ammonium be mixed with a solution of an alkaline tungstate, the brown tersulphide of tungsten (WoS_3) will be precipitated on the addition of acids; the supernatant liquid remains mostly colored blue, in consequence of the partial reduction of the tungstic acid.

Pure oxides of tungsten communicate to phosphate of ammonia-soda, in the inner flame of the blowpipe, a beautiful blue color (in the presence of iron a blood-red), which disappears in the outer flame. In the presence of tin, the bead containing iron becomes blue or green. Tungstic acid gives with borax, in the outer flame, a colorless bead; and a yellow, becoming dark yellow in the inner flame. The lower oxides of tungsten, by being heated in the air or with nitric acid are converted into tungstic acid; they yield the metal as a gray powder when ignited with soda and cyanide of potassium on charcoal.

The tungstates are easily recognized by their comportment with acids. If the minerals Wolfram or Tungsten, in a finely pulverized condition be treated with concentrated chlorhydric acid, with the addition of some nitric acid, the yellow tungstic acid will remain undissolved, which can easily be taken up by ammonia, and will acquire a blue color with zinc and chlorhydric acid.

In the analysis of Wolfram (or indeed any insoluble tungstate), the finely pulverized substance is digested with aqua-regia until there is complete decomposition, evaporated in a water bath to dryness, treated with acidulated water, and the tungstic acid washed out by means of alcohol. Tungstic acid thus obtained, on treatment with ammonia, leaves behind some niobic acid which is removed by filtration. The evaporated solution yields, on ignition in the air, tungstic acid. Or three parts of the washed mineral are fused along with two parts of carbonate of potassa and a half part of nitre in a platinum crucible, treated with water, and, after the solution has been nearly neutralized by the addition of nitric acid, the tungstic acid is precipitated by means of subnitrate of mercury, with the addition of a few drops of ammonia. The washed precipitate yields, after ignition, tungstic acid. The tungstates are also decomposed by being heated along with concentrated sulphuric acid, or bisulphate of potassa. Tungstic acid is separated from silicic acid (and niobic acid) by means of ammonia.

8. [Oxides of Molybdenum.]

Protoxide, MoO, *Binoxide*, MoO_2, and *Molybdic acid*, MoO_3.—Molybdenum is found as Molybdenite, MoS_2, and as Molybdate of lead, PbO, MoO_3. The salts of the protoxide and binoxide dissolve in water and in acids with black or reddish-brown colors, which become blue in the air. Both afford precipitates of a brown color with ammonia and the fixed alkalies, which are insoluble in excess of the precipitants, though soluble in carbonate of ammonia. The lower oxides, as also the bisulphide are converted into molybdic acid on being ignited in the air. The acid is a white powder, when heated lemon-yellow, and fusible at a red heat. The alkaline molybdates are soluble in water; from which solution, chlorhydric acid separates molybdic acid, which is again soluble in excess of the chlorhydric acid. *Zinc* produces, in such a solution, at first a blue, then a green color, and finally a black precipitate of the protoxide of molybdenum.

All the oxides of molybdenum in acid solutions gradually give a brown precipitate of the bisulphide with excess of *sulphydric acid*, whilst the supernatant liquid remains blue or green. This same precipitate is produced when the aqueous solution of an alkaline molybdate is mixed with *sulphide of ammonium* (or saturated with sulphydric acid) and then acidified with chlorhydric acid.

If a solution of molybdate of ammonia is mixed with a small quantity of a phosphate (or an arseniate), then with excess of nitric acid and warmed, the fluid will be yellow and there will also be a yellow precipitate. (See phosphoric acid.)

All the oxides of molybdenum give, in the inner flame of the blowpipe along with phosphate of ammonia-soda, beautiful green, and with borax brown pearls, which become in the outer flame yellowish green, yellow, or quite colorless. Molybdenite is converted into molybdic acid, which can be extracted by dilute ammonia, on being roasted in a crucible placed obliquely. In order to obtain molybdic acid from molybdate of lead, the latter should be finely pulverized and freed from carbonate of zinc, lime, and protoxide of iron, by judicious treatment with dilute chlorhydric acid, then heated along with $1\frac{1}{4}$ part of concentrated sulphuric acid, until it has become completely white, and the sulphuric acid begins to evaporate, mixed when cold with much water and the filtrate, with the addition of some nitric acid, evaporated in a porcelain dish with stirring, until the sulphuric acid begins to evaporate, when the molybdic acid is separated, which, after being washed, is freed at last from phosphoric acid by water containing some nitric acid. Or the ore which has been treated with dilute chlorhydric acid is decomposed by being heated with the concentrated acid, and the dry mass is treated with ammonia, and the filtrate evaporated down to crystallization, or being mixed with nitric acid it is evaporated to dryness and extracted with water, when the molybdic acid remains. Or the ore is fused with an equal weight of charred tartar (black flux), treated with water and evaporated to dryness after saturation with nitric acid. Molybdic acid remains after the nitrate of soda is removed by water.

In analysis, solutions of molybdic acid in dilute ammonia are precipitated by means of subnitrate of mercury, and the washed precipitate is then heated along with very dilute subnitrate of mercury, in an atmosphere of hydrogen, when the binoxide of Molybdenum, MoO_2, remains behind.

9. [Oxides of Tellurium.]

Tellurious acid, TeO_2 and *Telluric acid*, TeO_3.—Tellurium is found native or in combination with sulphur, gold, silver, bismuth, or lead. It is very fusible; heated in the air it burns with a bluish flame, forming a white smoke with a weak acid odor. Sulphuric acid acquires a beautiful amethystine-red color from contact with metallic tellurium at ordinary temperatures.

Tellurious acid is formed when the metal is dissolved in nitric acid, and *telluric acid*, when tellurious acid is fused along with nitre. Both are reduced, when ignited with carbonate of potassa and charcoal, to the telluride of potassium, which blackens polished silver, and evolves with acids telluretted hydrogen (HTe) resembling sulphydric acid gas in odor, and is soluble in water, giving it a wine-red color.

Solutions of the tellurious acids in mineral acids are precipitated white by water; the *caustic* and *carbonated alkalies* throw down the white hydrate, soluble in excess of precipitant; *sulphydric acid,* the blackish-brown bisulphate of tellurium TeS_2, very soluble in sulphide of ammonium.

Sulphurous acid (also the protochloride of tin and zinc) throw down the metal as a black powder; only at the temperature of ebullition and the precipitation is the more complete the more concentrated the solution is.

Telluric acid is converted into tellurious acid on being boiled with chlorhydric acid, and chlorine is evolved.

The compounds of tellurium are easily reduced on charcoal, in the inner flame of the blowpipe, accompanied with a white incrustation. If a telluride is heated in an open glass tube, tellurious acid sublimes as a white coating, fusible to colorless drops.

Tellurium ores containing gold, silver, and lead, are treated, in order to obtain their tellurium (after all their constituents soluble in dilute chlorhydric acid are removed) with aqua-regia, employing as little nitric acid as possible, sulphuric acid is added to the mass which has become white (for the removal of all the lead), and (to prevent the precipitation of tellurious acid) some tartaric acid, and double the volume of water; the gold is precipitated from the filtrate by protosulphate of iron, so that the tellurium can be removed from the concentrated solution by an alkaline sulphite. Or the purified compound ore, mixed with two parts of bisulphate of potassa, is projected by degrees into a Hessian crucible which contains six parts of bisulphate of potassa in a state of fusion, the mass which has become white is poured off from the gold, treated with water containing sulphuric acid, and the silver first precipitated from the filtrate by chlorhydric acid, and then the tellurium by sulphurous acid.

Telluride of bismuth is ignited with three parts of charred tartar (black flux) for an hour in a closed crucible, and the mass treated with water freed from air; the dark-red solution deposits, on standing in the air, all the tellurium.

10. [OXIDES OF SELENIUM.]

Selenious Acid, SeO_2 and *Selenic Acid*, SeO_3. — Selenium is found in combination with lead, iron, copper, mercury, and silver, in many iron and copper pyrites, and is removed from them by sulphuric acid (in Selenschlamm). It is reddish brown, of a dark leaden gray fracture, very fusible, burning in the air with a reddish-blue flame, forming selenious acid and protoxide of selenium, the latter of which diffuses a penetrating horse-radish odor. Selenious acid is formed on treating selenium with nitric acid or aqua-regia; it is soluble in water, and is crystallizable.

Sulphydric acid throws down from a solution of selenious acid, the orange-yellow bisulphide (SeS_2) which is soluble in sulphide of ammonium.

Sulphurous acid precipitates, especially on the application of heat, at first a red, and then a gray powder of selenium ($SeO_2 + 2SO_2 = Se + 2SO_3$). Zinc and iron reduce the copper-red selenium.

Selenic acid is formed by igniting selenium or selenious acid with nitre. Its salts comport themselves like the sulphates; however, on being boiled with chlorhydric acid, they yield chlorine and selenious acid, which can then be precipitated by sulphurous acid or sulphydric acid.

All the compounds of selenium, when ignited with soda on charcoal, yield the characteristic horse-radish odor and a residuum which blackens polished silver, and evolves selenietted hydrogen when mixed with acids. The selenites and seleniates, when ignited along with chloride of ammonium, give a sublimate of selenium, which the metallic selenides also furnish when heated in an open glass tube.

Selenium-sediment (selenschlamm) contains, besides selenium, selenide of mercury, selenites and seleniates, the sulphate of lead, silicic acid, etc. In order to remove the selenium therefrom, it is mixed with one fourth part of nitre, and heated with a mixture of equal parts of sulphuric acid and water until all the nitric acid has been volatilized, and the evaporated filtrate is then boiled with the addition (one half part) of chloride of sodium. The selenium is precipitated from the decanted liquid, when cold, by the introduction of sulphurous acid, the liquid being raised to ebullition towards the close. The selenium thus obtained, leaves behind, on distillation, small quantities of lead, iron, and copper, as selenides; it can be freed from mercury by re-solution in aqua-regia, saturating the liquid (freed from nitric acid) with carbonate of soda, and then igniting the dried salts. The solution of the latter is boiled with chlorhydric acid, and the selenium precipitated by sulphurous acid.

PART SECOND.

COMPORTMENT OF THE METALLOIDS AND THEIR MORE IMPORTANT COMPOUNDS.

1. The Acids of Sulphur.

Sulphur is found native, or as sulphydric acid (in sulphur springs), or in the metallic sulphides (called by the names of kies, glance, and blende, in mineralogy) or in the sulphates of a great number of the metallic oxides.

a. Sulphydric Acid SH (and the sulphides). — Sulphydric acid is a colorless gas, with an unpleasant odor (that of rotten eggs), burning with a blue flame; cold water absorbs about three times its volume of this gas (sulphydric acid water). Sulphydric acid transforms most of the metallic oxides at higher temperatures, or in aqueous solution, into water and sulphides which mostly have characteristic colors. The compounds of sulphur with the metals of the alkalies and alkaline earths are soluble in water, but those with the heavy metals are insoluble therein. But few of the sulphides, when heated under exclusion of air, lose their sulphur (the sulphide of gold and of platinum), some of the higher sulphides, on such exposure, only give off a portion of their sulphur (bisulphide of iron, quinquesulphide of antimony, etc.). All the sulphides evolve sulphurous acid on ignition in the air; some leaving behind the metal (silver), others the oxide (tin, antimony, bismuth, molybdenum), and others are converted into the sulphates (as the alkaline sulphides and those of the alkaline earths, the sulphides of copper, lead, etc.).

Some of the sulphides are soluble in dilute chlorhydric acid, with the evolution of sulphydric acid gas (sulphides of the alkalies and alkaline earths, those of iron, manganese, zinc, and uranium), others require concentrated acids (the sulphides of nickel, cobalt, antimony, and lead), and others again are insoluble even in concentrated chlorhydric acid (the sulphides of arsenic, copper, mercury, gold, platinum, etc.).

All the sulphides are decomposed by digestion with concentrated nitric acid or aqua-regia, or chlorhydric acid and chlorate of potassa, with the formation of sulphuric acid, the oxide or chloride of the metal, and, if the acid reagent is not sufficiently concentrated, or has not acted for a sufficient length of time, with even the separation of the sulphur.

Protosulphide of mercury is not decomposed by pure nitric acid, though easily effected by aqua-regia; sulphide of lead is converted by nitric acid into the sulphate, sulphide of tin into the binoxide, sulphide of antimony into the teroxide of antimony or antimonic acid. All the sulphides, when heated in chlorine gas, are resolved into metallic chlorides and a chloride of sulphur.

Those sulphides, which are soluble in water, are divided into the *protosulphides* (KS, NaS, NH_4S, BaS); *sulphydrated-sulphides* (KS, HS; NH_4S, HS, etc.), and the *poly-sulphides* (KS_5, NH_4S_5, etc.). The aqueous solutions of the first and second are colorless, and evolve sulphydric acid on the addition of acids, without the precipitation of sulphur; those of the last are yellow or yellowish-brown, and evolve sulphydric acid on the addition of acids, but at the same time precipitate sulphur.

The soluble protosulphides give, with the neutral protosulphate of manganese, a precipitate of the sulphide of manganese, without the evolution of sulphydric acid; the sulphydrated sulphides disengage, under similar circumstances, the second atom of sulphur in the form of sulphydric acid gas. All the soluble sulphides (and also many of those insoluble in water) are decomposed very quickly in the air, with the absorption of oxygen. The colorless solutions of the protosulphides, and the sulphydrated sulphides become first yellow, with the formation of the quinque-sulphides ($5\,KS + 4\,O = KS_5 + 4\,KO$), then the hyposulphite is formed ($KS_5, 4KO + 6\,O = 5\,(KO, SO)$), and finally from the absorption of still more oxygen, a sulphite and a sulphate. The sulphydrated-sulphides are only oxidized so as to form hyposulphites ($4\,KS, HS + 4\,O = KO, S_2O_2 + HO$); the solutions of the quinque-sulphides are gradually decolorized in the air, sulphur is precipitated in the absence of free alkali, and a hyposulphite is formed ($KS_5 + 3\,O = KO, S_2O_2 + 3\,S$). Sulphydric acid water loses its odor on exposure to the air, and sulphur is precipitated ($SH + O = HO + S$).

The presence of sulphydric acid, or of a soluble sulphide, is recognized (in neutral, acid, or even alkaline solutions) by the black precipitate of the sulphide of lead, produced by *solutions of lead;* the smallest quantity of sulphydric acid is detected by a piece of paper moistened with acetate of lead, whether it is disengaged separately or in a mixture of gases; the paper is blackened, or is covered with a dark-brown shining coating of sulphide of lead. The gas is completely absorbed by potassa-lye, or by ammonia.

Nitro-ferricyanide of sodium produces no change of color in sulphydric acid water, or in acid fluids containing sulphydric acid ; yet if there be small quantities of a soluble sulphide present, even in the presence of free sulphydric acid, they can be recognized by the splendid blue, and then purple-red transient colors, which a slight addition of the nitro-ferricyanide of sodium produces in the fluid to be tested. This is an exact method of distinguishing whether a fluid contains a soluble sulphide along with free sulphydric acid. When there is great dilution, the color does not appear instantaneously.

An alcoholic solution of *iodine* (or still better, an aqueous solution of iodine in iodide of potassium) is instantly converted into iodhydric acid, by the agency of sulphydric acid, and sulphur is disengaged which renders the fluid milky ($I + HS = HI + S$). If an iodine solution of a determined strength be employed for this purpose, and the fluid to be tested be mixed with some starch paste, the point can be determined with certainty by the appearance of the blue color when all the sulphydric acid is decomposed. The amount of sulphydric acid is calculated by the amount of iodine solution used. The soluble sulphides comport themselves similarly with iodine. Alkaline fluids should be neutralized with acetic acid, before using this proof.

Chlorine and *bromine*, as well as *sulphurous*, *hypochlorous*, and *nitrous acid*, *iodic acid*, *chromic acid*, *the sesquisalts of iron*, etc., likewise decompose sulphydric acid with the separation of sulphur, and, as a rule, with the formation of some sulphuric acid. (For the detection of metallic sulphides before blowpipe, see page 117.)

b. SULPHURIC ACID, SO_3. — Anhydrous sulphuric acid (SO_3) is a solid substance resembling asbestos, producing, on exposure to the air, suffocating white fumes ; the hydrate (SO_3, HO) is an oily liquid, very acid and caustic, boiling at 327° C. Both forms mix with water, producing much heat. Sulphuric acid shows the strongest affinity for bases, on which account it is used for the separation of all the other acids from their salts. The neutral and the acid sulphates are almost all soluble in water; those which are basic are insoluble in water, though soluble in acids. The sulphate of lime is with difficulty soluble in water (requiring 500 parts), still more so the sulphate of strontia (9,000 parts), and the sulphate of lead (22,000 parts); the sulphate of baryta is almost perfectly insoluble in water.

For the sure detection and determination of sulphuric acid in compounds which are soluble in water or in acids, it is necessary to add to the fluid to be tested, being previously acidified by chlorhydric acid, *the chloride of barium*, or *the nitrate of baryta*. The resulting white, pulverulent precipitate of the sulphate of baryta ($Ba\,O, S\,O_3$) is slightly soluble in nitric or chlorhydric acid. Care must be taken in using this reaction that the fluid do not contain too much free chlorhydric or nitric acid, since the chloride of barium itself, and, still more, the nitrate of baryta are with difficulty soluble in very acid liquids. But the precipitate arising from the latter salt is readily dissolved on the addition of water, while the sulphate of baryta does not disappear even in a great quantity of water. For the detection of very small quantities of sulphuric acid (in nitric acid solutions especially) it is necessary that the fluid mixed with the baryta salt should be allowed to stand for some time. The sulphate of baryta precipitated in the presence of free nitric acid, or a nitrate, takes with it generally some nitrate of baryta, which cannot be removed by washing with water. It must, in a quantitive analysis, be treated with chlorhydric acid, after its ignition, and again be washed with water. Freshly precipitated sulphate of baryta will generally pass cloudy through the filter; if the acid fluid is boiled for a short time with the precipitate, a clear filtrate can be obtained.

The sulphates are insoluble in alcohol; lime, strontia, and protoxide of lead are completely precipitated in the presence of alcohol by sulphuric acid; the sulphate of lead is with more difficulty soluble in water containing sulphuric acid (requiring 36,500 parts) than in that which is pure. The compounds of sulphuric acid with the fixed alkalies, the alkaline earths, and with protoxide of lead are not decomposed when ignited by themselves; all the other sulphates are decomposed in this way, whilst according to the nature of the base, sometimes sulphuric acid, or again sulphurous acid and oxygen are disengaged. All the sulphates are decomposed by ignition along with charcoal; the sulphates of the alkalies and alkaline earths are resolved into soluble metallic sulphides; the other sulphates disengage sulphurous acid.

The sulphates which are insoluble in water and in acids are completely decomposed by fusion along with the alkaline carbonates, but only partially on boiling with a concentrated aqueous solution of them. (E. g. $BaO, SO_3 + NaO, CO_2 = BaO, CO_2 + NaO, SO_3$). The fused mass is treated with hot water (not with acids), filtered, and the filtrate saturated with chlorhydric acid, so that the sulphuric acid can now be tested by means of chloride of barium. The residue will contain the base, which was united to the sulphuric acid, as a carbonate.

For the detection of sulphuric acid before the blowpipe flame, see page 117. Seleniate of baryta is decomposed by being boiled with strong chlorhydric acid, chlorine being disengaged and selenious acid formed; or by ignition in hydrogen gas, it is resolved into selenide of barium, which is soluble in chlorhydric acid. Under these circumstances, sulphate of baryta suffers no decomposition.

c. SULPHUROUS ACID, SO_2. This acid is formed in burning sulphur, or roasting the metallic sulphides, by the deoxidation of sulphuric acid by the agency of charcoal or organic compounds, or many of the metals, etc. It is a gas at ordinary temperatures, readily absorbed by water, imparting an unpleasant, suffocating odor — that of burning sulphur. The alkaline sulphites are the only neutral sulphites which are soluble in water; those which are insoluble in water are, however, readily soluble in sulphurous or chlorhydric acid; their solutions slowly absorb oxygen from the air, with the formation of sulphuric acid. By heating with concentrated nitric acid, or by chlorine, hypochlorous acid or iodine, they are immediately converted into sulphates, without the precipitation of the sulphur.

Chloride of barium gives, with the sulphites, a white, pulverulent precipitate, insoluble in water, though readily soluble in chlorhydric acid. This solution parts with the sulphate of baryta immediately on the addition of hypochlorite of soda, or the chlorate of potassa or iodine.

Acetate of lead throws down the white sulphite of lead, very soluble in dilute nitric acid.

Nitrate of silver gives a white precipitate, which blackens on boiling, on account of the reduction of the metal; the fluid then contains sulphuric acid.

Subnitrate of mercury gives a gray precipitate of metallic mercury.

Sulphurous acid is a powerful reducing agent; it precipitates brown metallic gold, from the terchloride, it converts chromic acid immediately into the green sesquioxide of chromium, arsenic acid (being heated for some time) into arsenious acid, the sesquisalts of iron into the protosalts, tellurious acid, or selenious acid, into metallic tellurium or selenium, etc.

Metallic zinc is soluble in sulphurous acid without the development of gas ($2\,Zn + 3\,SO_2 = ZnO, S_2O_2 + ZnO, SO_2$); in the presence of chlorhydric acid, sulphurous acid develops sulphydric acid, recognizable by lead paper. By this reaction the smallest quantities of sulphurous acid (in chlorhydric acid for example) can be detected. Some of the following acids of sulphur comport themselves in this manner. Along with sulphydric acid, the aqueous solution of sulphurous acid is decomposed, sulphur is precipitated and pentathionic acid is formed.

If a solution of sulphurous acid is heated along with protochloride of tin and chlorhydric acid, the yellow protosulphide of tin is gradually precipitated; by the addition of one drop of a soluble protosalt of copper this reaction becomes more perceptible (in consequence of the formation of the black sulphide of copper).

Sulphurous acid is easily and completely absorbed by the peroxide of lead ($PbO_2 + SO_2 = PbO, SO_3$). If a glass rod moistened with starch paste, and a solution of iodide of potassium be introduced in a gaseous mixture which contains sulphurous acid, the blue iodide of starch will immediately be formed.

Most of the sulphites are resolved, on being heated, into the sulphates and the sulphides ($4\,(KO, SO_2) = 3\,(KO, SO_3) + KS$); the sulphites of the earths evolve sulphurous acid, and leave their oxides behind. They comport themselves before the blowpipe as the other compounds of sulphur (see page 117).

Sulphurous acid is the only oxygen compound of sulphur, which is converted by iodine into sulphuric acid, which comportment may serve for its recognition, and (with the use of a titrited solution of iodine) for its quantitative determination. If sulphuric acid be present at the same time, it must be first precipitated by chloride of barium in the presence of free chlorhydric acid.

d. DITHIONOUS ACID. (*Hyposulphurous acid*) S_2O_2.—Dithionous acid is produced on digesting a sulphite along with sulphur, by the oxidation of the soluble sulphides in the air, and along with a metallic sulphide in solutions of sulphur in alkaline oxides, etc. It is only known in combination with bases; in a free condition it is resolved (immediately in a concentrated solution, or slowly in one that is dilute) into sulphurous acid and sulphur, the latter of which is deposited ($S_2O_2 = SO_2 + S$). Nearly all the dithionites are soluble in water; their solutions give white precipitates, with *the salts of the protoxides of lead, mercury,* and *silver,* which become (especially on being warmed) yellow, brown, and then black, on account of the formation of the sulphide and sulphuric acid ($AgO, S_2O_2 = AgS + SO_3$).

Protochloride of tin gives a brown precipitate, and the *subnitrate of mercury* immediately a black.

The dithionites dissolve chloride of silver, subchloride of mercury, and sulphate of lead. Warmed with chlorhydric acid, they disengage sulphurous acid, and sulphur is thrown down; with iodine there is produced an iodide and a tetrathionate ($2(BaO, S_2O_2) + I = BaI + BaO, S_4O_5$), which action distinguishes them from sulphurous acid; with hypochlorite of soda (or chlorine) all the contained sulphur is converted into sulphuric acid, even at ordinary temperatures ($NaO, S_2O_2 + 4HO + 4Cl = NaO, 2SO_3 + 4HCl$). At higher temperatures, the dithionites are resolved into a sulphide and a sulphate, while a portion of the sulphur escapes; $4(KO, S_2O_2) =$

$KS_5 + 3 (KO, SO_3)$. They comport themselves with zinc and chlorhydric acid as the sulphites. For comportment before the blowpipe, see page 116.

Dithionous acid can be recognized when along with sulphydric acid (or a soluble sulphide), since the neutral fluid can be precipitated with a neutral salt of zinc; after the removal by filtration of the sulphide of zinc, the fluid will show the reactions of dithionous acid.

e. Dithionic Acid. (*Hyposulphuric acid*) S_2O_5. — Is produced (along with sulphuric acid) by the action of binoxide of manganese on aqueous solutions of sulphurous acid ($MnO_2 + 2 SO_2 = MnO, S_2O_5$). Its salts are all soluble in water and are not precipitated, on this account, by any metallic salt. Its solutions do not give sulphuric acid, along with hypochlorite of soda when cold; after being boiled with nitric acid or chlorhydric acid and chlorate of potassa, they yield, with chloride of barium, a precipitate of the sulphate of baryta. The dry salts are decomposed by concentrated sulphuric acid, only when heated, with the disengagement of sulphurous acid; on ignition they are resolved into a sulphate which remains behind, and sulphurous acid which escapes. Dithionic acid is easily distinguished from sulphuric acid and sulphurous acid by the solubility of its baryta salt; from the polythionic acids, because in its decomposition by acids there is no separation of sulphur, and the salts of silver and mercury produce no precipitates with it.

f. Trithionic Acid, S_3O_5. — This is produced, along with dithionous acid (and sulphuric acid) on digesting acid sulphites along with sulphur, or by passing sulphurous acid into the sulphide of potassium. The free acid is more permanent than dithionous acid; on heating its aqueous solution to ebullition, it is resolved into sulphuric acid, sulphurous acid, and sulphur, without the disengagement of sulphydric acid; its salts comport themselves in like manner; the acid, on long boiling with potassa, is resolved into a sulphite (or a sulphate) and a dithionite ($2\,S_3O_5 + 5\,KO = 4\,(KO, SO_2) + KO, S_2O_2$); the liquid will not then give a precipitate of the sulphide of lead with the salts of lead. By hypochlorous acid (or chlorine) all the contained sulphur is converted into sulphuric acid ($KO, S_3O_5 + 4\,HO + 4\,Cl = KO, 3\,SO_3 + 4\,HCl$).

Solutions of the trithionates give a black precipitate immediately with the *subnitrate of mercury*, with *nitrate of silver* a white precipitate which soon blackens; in the presence of ammonia, no precipitate is produced.

Chloride of mercury gives a pure white, and *cyanide of mercury* a yellowish precipitate.

The salts of baryta and lime, as also those of lead are not precipitated by this acid; when it is heated with excess of protosulphate of copper, the sulphide of copper is immediately thrown down.

g. TETRATHIONIC ACID, S_4O_5. — This acid is produced by the action of iodine on a dithionite (p. 113). The acid, when uncombined, is more permanent than when in the presence of strong bases; its aqueous solution is not decomposed at the boiling point; on boiling with potassa, it is resolved into the sulphite and dithionite of potassa, together with the sulphide of potassium, on which account the solution gives, with the salts of lead, a black precipitate.

With *subnitrate of mercury* there is produced a yellow precipitate, becoming black on boiling. *Chloride of mercury* and *nitrate of silver* give yellowish precipitates.

There is no precipitate produced with the salts of baryta and lead; with the salts of copper, on long boiling, there is formed a brown precipitate. The whole of the sulphur compound is converted by hypochlorite of soda (or chlorine) into sulphuric acid; ($KO, S_4O_5 + 4HO + 7Cl = KO, 4SO_3 + 7HCl$).

h. Pentathionic Acid, S_5O_5.—This is produced by the action of sulphydric acid on aqueous sulphurous acid. It comports itself very like tetrathionic acid, and is distinguished from it by the fact that the nitrate of ammonia-silver immediately produces in pentathionic acid, saturated with ammonia, a brown precipitate, which gradually passes into the condition of the sulphide of silver.

Pentathionic acid, when boiled with potassa, is resolved into the dithionite of potassa along with some sulphide of potassium; all its sulphur is converted into sulphuric acid by means of hypochlorite of soda ($KO, S_5O_5 + 10Cl + 10HO = (KO, 5SO_3 + 10HCl$).

All the polythionic acids or their salts are decomposed by being boiled along with cyanide of mercury, and cyanhydric acid is disengaged; there will be formed always under these circumstances, for each equivalent of sulphide of mercury, two equivalents of sulphuric acid; with tetrathionic acid, there is mixed with the sulphide, one equivalent of sulphur, and with pentathionic acid, two equivalents; dithionous acid yields only one equivalent of sulphuric acid for each equivalent of the sulphide.

Detection of sulphur in the dry way and before the blowpipe.—Pure sulphur melts when heated on platinum foil, and is completely volatilized; it burns with a blue flame, being converted into sulphurous acid, which is easily recognized by its odor. All the compounds of sulphur already treated of or their salts, without exception, yield, when ignited in a charcoal cavity, before the reduction flame, with soda (or with one part of borax and two parts of soda) the liver of sulphur (hepar), recognizable by the fact that the ignited mass along with acids evolves sulphydric acid, or, after it has been moistened, occasions a blackish-brown spot on polished silver. If an organic compound is to be examined for sulphur, it is fused along with hydrate of potassa on silver foil, when, after its solution in water, a black spot remains; or it is decomposed by nitric acid, chlorhydric acid, and chlorate of potassa, or by fusion with carbonated or caustic alkali (free from sulphuric acid) and nitre, and then the acid solution is tested for sulphuric acid by the chloride of barium. Some organic compounds containing sulphur are decomposed by boiling with strong potassa-lye, with the formation of sulphide of potassium; the salts of lead would then produce in the alkaline liquid a black precipitate.

If a soda pearl, saturated with silicic acid on a platinum wire, be exposed along with any compound of sulphur in the reduction flame, according to the quantity of sulphur in the mixture, there will be a yellow, yellowish-brown, or reddish-brown bead.

2. The Acids of Phosphorus.

Phosphorus is very abundant in nature, but only indeed in the form of the tribasic phosphoric acid, in combination with lime, magnesia, sesquioxide of iron, alumina, protoxide of lead, protoxide of copper, etc.; it is found also, in all organisms, mostly accompanied by the fluorides.

a. Common or Tribasic Phosphoric Acid, $PO_5, 3HO$. — Common phosphoric acid forms crystals as clear as water or a syrupy liquid, which passes at a higher temperature, with loss of water, into pyro- and metaphosphoric acid. When melted in an uncovered platinum crucible at a red heat, it is volatile. It is very soluble in water and alcohol. Its aqueous solution has a strong acid reaction, and gives no precipitate with a solution of *albumen*, or of *chloride of barium*; excess of *lime* or *baryta water* produces a white precipitate.

The alkaline phosphates are readily soluble in water with an alkaline reaction; all the other common phosphates are either insoluble or with difficulty soluble in water; all are soluble in nitric or chlorhydric acid; the phosphates of the alkaline earths, when freshly precipitated, are also soluble in acetic acid. The solution of the phosphate of an alkaline earth in an acid, when neutralized with an alkali, gives a precipitate of the phosphate unchanged, and insoluble in excess of the alkali. Those phosphates which are insoluble in water are generally soluble in an excess of the saline solution, in which they would be precipitated by phosphate of soda; this solution is turbid on being strongly heated, but becomes again clear when cold.

Nitrate of silver gives a yellow precipitate (PO_5, $3AgO$) with the soluble common phosphates, soluble in nitric acid and in ammonia. *Acetate of lead* gives a white precipitate (PO_5, $3PbO$), insoluble in ammonia and in acetic acid, though soluble in nitric acid; in the presence of a chloride the precipitate contains chloride of lead in chemical combination; if the precipitate is fused before the blowpipe, the pearl becomes crystalline and angular when cold.

Chloride of barium and *chloride of calcium* give white precipitates ($2BaO$, HO, PO_5 and $2CaO$, HO, PO_5), readily soluble in chlorhydric or nitric acid, and in acetic acid; the phosphate of lime separates in a crystalline form from the solution in acetic acid, after some time, particularly if heat has been employed, and in an excess of the phosphate; it is further somewhat soluble in water containing carbonic acid and in ammoniacal salts, also in the presence of free ammonia; from its solution in acetic acid (or its solution in chlorhydric acid, mixed with acetate of soda) the whole of the lime is precipitated, by oxalate of ammonia, as an oxalate, and from its chlorhydric or nitric acid solution, by sulphuric acid and alcohol, as a sulphate. (Determination of lime in ashes and in bone earth.)

A mixture of *sulphate of magnesia* (or chloride of magnesium) with chloride of ammonium and ammonia gives, with the soluble phosphates, a crystalline precipitate ($2\,MgO, NH_4O, PO_5 + 12$ aq.) readily soluble in all the acids, somewhat soluble in pure water, completely insoluble (even in the presence of a large quantity of an ammoniacal salt) in water containing free ammonia. This precipitate, which becomes after ignition $2\,MgO, PO_5$, serves for the detection and determination of phosphoric acid (in the absence of arsenic acid) in all compounds which are soluble in water, and whose watery solutions are not made turbid by the addition of ammonia and chloride of ammonium. It is only slowly formed in very dilute fluids; if it is precipitated in a solution which contains tartaric acid and sesquioxide of iron, there will be probably mixed with it some tartrate of magnesia and sesquioxide of iron.

Sesquichloride of iron gives a yellowish white precipitate (Fe_2O_3, PO_5) soluble in chlorhydric acid, excess of sesquichloride of iron, acetate of the sesquioxide of iron, and in ammonia. This precipitate is quite insoluble in acetic acid, on which account it is produced if its solution in chlorhydric acid is mixed with acetate of soda, or if a solution of a phosphate of an alkaline earth is mixed with a *little* of the sesquichloride of iron and acetate of soda. If to the chlorhydric acid solution of any compound of phosphoric acid (after the excess of acid has been neutralized by ammonia or carbonate of soda) there be added acetate of soda, and then the sesquichloride of iron in small excess (which is known when the fluid becomes reddish), and the mixture be then heated to ebullition, the reddish-brown precipitate produced contains *all* the phosphoric acid and *all* the sesquioxide of iron; it must be filtered off while hot, and be washed out with hot water. Arsenic acid in this respect comports itself exactly as phosphoric acid, and alumina also is precipitated under these circumstances, but not so completely. (On this reaction, depends an easy and exact method for the determination of phosphoric acid by the employment of a determined volume of sesquichloride of iron of known strength, also for its complete removal (or that of the sesquioxide of iron) from solutions, in which lime, magnesia, protoxide of manganese, or the isomorphous oxides are still to be determined).

Nitrate of the sesquioxide of uranium comports itself like the sesquichloride of iron in solutions of the phosphates.

Subnitrate of mercury produces a white precipitate in aqueous solutions of the phosphates, which is very soluble in nitric acid. When the nitric acid solution of a phosphate (containing an adequate amount of free nitric acid) is evaporated (in the presence of excess of metallic mercury) in a water bath, down to perfect dryness, and the dry residue (freed from acid) treated with water, all the metallic oxides which had existed in combination with phosphoric acid are dissolved out as nitrates, while the whole of the phosphoric acid remains, in combination with the suboxide of mercury, insoluble. Henry Rosé uses this reaction for the separation of phosphoric acid from all the bases, except alumina. In the part which is insoluble in water, the phosphoric acid is determined as phosphate of ammonia-magnesia (after the mercury has been driven away by gentle ignition with the carbonate of soda-potassa); the mercury can be removed from the portion which is soluble in water by chlorhydric acid and ammonia, or by evaporation and gentle ignition. If sesquioxide of iron is present, a part will be found in the soluble, and a part in the insoluble portion.

For the detection of very small quantities of phosphoric acid, the *molybdate of ammonia* can be most judiciously employed. The solution of a phosphate, when mixed with molybdate of ammonia, and then with excess of chlorhydric acid, or still better, with nitric acid, and warmed, will be colored yellow, and then will appear either directly or after some time, a yellow precipitate of the molybdate of ammonia containing the phosphoric acid (which is soluble in ammonia as well as in an excess of the phosphate), on which account this reaction is specially fitted for the recognition of very small quantities of phosphoric acid (in fossils, soils, and the deposits of mineral springs). Arsenic acid shows a similar reaction.

Those phosphates which have three equivalents of fixed base undergo no decomposition when ignited by themselves; those with two equivalents of fixed base become pyrophosphates, and those with one equivalent are converted into metaphosphates. By fusion along with carbonate of soda-potassa, the phosphates of baryta, strontia, and lime are only imperfectly decomposed; most of the remaining insoluble phosphates (protophosphate of magnesia, zinc, manganese, and of copper, and the sesquiphosphate of iron) are thereby completely decomposed; the fused mass always contains the phosphoric acid in tribasic form. The insoluble phosphates, on being boiled with a solution of a caustic or carbonated alkali, are either only imperfectly or not at all decomposed. Phosphate of alumina is completely decomposed only by fusion along with an equal weight of silica, and six times the weight of carbonate of soda; the silica is removed from the aqueous solution of the residue by carbonate of ammonia, and then the phosphoric acid is precipitated as the phosphate of ammonia-magnesia, after the acidulation of the filtrate by chlorhydric acid, and its saturation by ammonia.

A solution of the phosphate of iron, the phosphate of magnesia, the phosphate of alumina, etc., in chlorhydric acid, will give up its phosphoric acid completely on digestion with excess of carbonate of baryta; weak bases — as oxides of the formula of M_2O_3 — are precipitated in this way. Phosphoric acid can be completely separated from baryta, strontia, and protoxide of lead by means of sulphuric acid, or from lime by means of sulphuric acid and alcohol. Phosphate of lead diffused through water is decomposed by sulphydric acid, and the freshly precipitated phosphate of the sesquioxide of iron by sulphide of ammonium; the filtrate in either case contains all the phosphoric acid.

For the exact separation of small quantities of phosphoric acid from a large quantity of sesquioxide of iron (even in the presence of lime and magnesia), the solution of the compound in chlorhydric acid is heated to ebullition along with the sulphite of soda, until all the sesquioxide of iron is reduced to the protoxide; afterwards all the sulphurous acid is driven away by boiling, the solution is neutralized with carbonate of soda, mixed with a small quantity of chlorine water (to form the sesquioxide of iron) and an excess of acetate of soda,

Fe_2O_3 + NaO SO_2 = 2 FeO + NaO SO_3

whereby the smallest quantity of phosphoric acid can be recognized by the precipitation of the white phosphate of the sesquioxide of iron; chlorine water is now added by drops, until the fluid appears reddish, when it is heated to ebullition and filtered. The precipitate containing all the phosphoric acid is either decomposed by sulphide of ammonium, or its solution in chlorhydric acid is heated along with sulphite of soda, mixed with excess of soda-lye, and boiled until it has become the black oxide ($FeO + F_2O_2$); the phosphoric acid is thrown down from the filtrate as the phosphate of ammonia-magnesia.

For the separation of phosphoric acid from alumina, the compound is dissolved in soda-lye, and the acid precipitated from the dilute solution, by chloride of barium or baryta water, as phosphate of baryta, during which precipitation, it is heated nearly to ebullition with the addition of more soda-lye and some carbonate of soda; the filtrate contains all the alumina. The phosphate of baryta is dissolved in chlorhydric acid, the baryta is precipitated by means of sulphuric acid, and the phosphoric acid is removed from the filtrate as the phosphate of ammonia-magnesia. If the sesquioxide of iron is present at the same time, it is reduced, before the treatment with caustic soda,* by sulphurous acid as described above.

Phosphoric acid is readily distinguished from sulphuric acid by the solubility of the baryta salt of the former in acids. A mixture of *chloride of ammonium, ammonia,* and a *magnesia-salt* answers particularly well for its detection in *neutral* or *alkaline* solutions; *the sesquichloride of*

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[*] In boiling alkaline fluids in glass or porcelain vessels, a not inconsiderable quantity of silica is taken up in the solution, on which account, in delicate investigations, platinum vessels should be used.

iron and *acetate of soda* in *acid* solutions; but the most delicate test for phosphoric acid is the *molybdate of ammonia.* Since arsenic acid conducts itself, in all these reactions, exactly as phosphoric acid, it is necessary to show by a special examination that the former is absent; they can be easily separated from each other in a warm *acid* solution by sulphydric acid.

If a dry phosphate be heated to low redness in a glass tube with three times the quantity of potassium or sodium, and then be warmed along with excess of mercury and the amalgam be slightly moistened (by breathing on it), there will be developed the characteristic odor of phosphoretted hydrogen. By this means very small quantities of phosphoric acid in dry compounds may be discovered.

If an iron wire be passed through the melted glass, formed by fusing a phosphate along with boracic acid on charcoal before the blowpipe flame, there will be formed in the inner flame, with a strong blast, a brittle globule of phosphide of iron.

b. PYROPHOSPHORIC ACID, $PO_5, 2HO$. — This acid is produced when the common phosphoric acid is heated to 213° C., or when the common phosphates, with two equivalents of fixed base are ignited. It is a viscous, acid syrup, whose solution is neither precipitated by *albumen* nor by *chloride of barium.* The alkaline pyrophosphates are soluble in water, and possess alkaline reactions, — the other pyrophosphates are insoluble in water, though soluble in acids, as also mostly in an excess of phosphate of soda, with the formation of soluble double salts, some of which behave peculiarly towards reagents. Thus in the solution of the phosphate of the sesquioxide of iron, or of the protoxide of manganese in the pyrophosphate of soda, the heavy metal is either with difficulty or not at all precipitated by sulphydric acid or the sulphide of ammonium.

The phosphates, which are insoluble in water, are soluble, as the common phosphates, in an excess of the salt of the metallic oxide from which they have been precipitated; the precipitate produced by heating this solution does not disappear on its being cooled.

Nitrate of silver gives a white precipitate ($2\,AgO, PO_5$) with the pyrophosphate of soda. The compounds of pyrophosphoric acid with the alkaline earths are with difficulty soluble in acetic acid. Pyrophosphoric acid, by itself as in its salts, is readily converted into the common tribasic modification, by being heated along with concentrated acids; the same occurs on fusing it with an excess of an alkaline carbonate; or if the latter be used in too small quantity there are produced double salts of common phosphoric acid, containing some alkali and insoluble in water, which is to be considered in the analyses of ashes.

c. METAPHOSPHORIC ACID, PO_5, HO, AND ITS POLYMERIC MODIFICATIONS.—The acid, PO_5, is produced on the rapid combustion of phosphorus, in the form of anhydrous snowy flakes, soluble in water, making an acid solution which strongly precipitates *albumen*, and gives with *nitrate of silver* a white precipitate, and with *chloride of barium*, one very voluminous. The other modifications of metaphosphoric acid likewise precipitate albumen (their soluble salts producing this effect on the addition of acetic acid), but a part of them produce no precipitate with the chloride of barium. The salts of one modification are—also those of the alkalies—all insoluble in water (MO, PO_5); those of the second ($2\,MO, 2\,PO_5$), and the third ($3\,MO, 3\,PO_5$), are soluble and crystallizable. Those of the fourth ($4\,MO, 4\,PO_5$) are tough, transparent masses;

the soda-salt of the fifth ($6\,MO, 6\,PO_5$), is deliquescent; the silver-salt is insoluble in water, but soluble in the soda-salt.

Some of these form double salts, which comport themselves as the pyrophosphates; all the modifications of metaphosphoric acid are converted into tribasic phosphoric acid by being heated for a long time with concentrated acids, or on fusion along with an alkaline carbonate.

Metaphosphoric acid is most certainly recognized by its comportment towards a solution of albumen. Along with molybdate of ammonia it first shows a yellow color, and a precipitate when by the action of free nitric acid, the common phosphoric acid has been produced. Metaphosphate of silver is soluble in excess of metaphosphate of soda; pyrophosphate of silver is insoluble in excess of pyrophosphate of soda.

If a small piece of metallic zinc is added to a melting pearl of metaphosphate of soda, or even of glacial phosphoric acid, on charcoal, there will break forth a little flame of briskly burning phosphorus on account of the partial reduction of the phosphoric acid.

d. Phosphorous Acid, PO_3.—This is formed in the slow combustion of phosphorus. When anhydrous, it is a white powder with a garlicky odor, when a hydrate, a syrupy liquid, crystallizing with difficulty, which, by boiling and fusion is converted into phosphoric acid with the liberation of phosphoretted hydrogen ($4\,PO_3 + 3\,HO = PH_3 + 3\,PO_5$).

The alkaline phosphites are soluble in water; the other salts of this acid are with difficulty soluble. On treatment with nitric acid or chlorine, they are converted into phosphates.

Solutions of phosphorous acid or of the alkaline phosphites are precipitated white by *chloride of barium* or *chloride of calcium*, which precipitate is soluble in acetic acid; *acetate of lead* throws down a white precipitate, insoluble in acetic acid; the salts of magnesia give no precipitate in a dilute solution.

The salts of most of the precious metals (nitrate of silver, subnitrate of mercury, and terchloride of gold) are readily reduced to their metallic condition by phosphorus acid, on saturation with ammonia.

With *protochloride of mercury* there is formed a white precipitate of the subchloride of mercury, Hg_2Cl; *sulphurous acid* yields, when warmed with phosphorous acid, a precipitate of sulphur, and, when an excess of the latter acid is used, sulphydric acid ($3\,PO_3 + 2\,SO_2 + 2\,HO = 3\,PO_5 + 2\,HS$; and $SO_2 + 2\,HS = 2\,HO + 3\,S$). If the phosphorous acid contains arsenic, this is completely precipitated as a sulphide of the metal.

Arsenic acid, when boiled with phosphorous acid, is converted into arsenious acid, and this, on fusion, is reduced to the metallic condition, which separates as a blackish brown powder.

Zinc and iron are soluble in phosphorous acid, with the liberation of *phosphoretted hydrogen.* The dry phosphites, on being heated in a glass tube, yield hydrogen (some also phosphoretted hydrogen), and a phosphate is left behind.

e. Hypophosphorous Acid, PO.—This is formed along with phosphoric acid and phosphoretted hydrogen when phosphorus is boiled with an alkaline oxide. Its salts are all soluble in water. They furnish with *nitrate of silver* a white precipitate, soon becoming the brown or black metal; with *acetate of lead*, as also with *baryta* and *lime water*, there is produced no precipitate. The hypophosphites are resolved into phosphoric acid, and phosphoretted hydrogen on being heated.

Phosphoretted hydrogen, PH_3, is a very inflammable, colorless gas, with a strong alliaceous odor; it is completely absorbed by nitrate of silver, the metal being precipitated; it affords a black precipitate in the salts of lead and copper, and a yellow, with the protochloride of mercury.

Phosphorus is luminous in the dark, inflames very readily, is not soluble in water, very slightly soluble in alcohol or ether, more readily in bisulphide of carbon; it is converted into phosphorous and phosphoric acid by oxidizing agents. Very small quantities of *free* phosphorus (as in poisoning by this substance), mixed with organic matters, can be most certainly indicated if the pap-like substances are mixed with water and some chlorhydric acid in a porcelain bowl, then warmed, being constantly stirred, up to the melting point of phosphorus, and after the mixture has settled, the supernatant liquid is poured off in perfect darkness. The smallest pieces of phosphorus can be recognized by their luminosity.

3. Oxides of Nitrogen.

a. Nitric Acid, NO_5, HO. — Pure hydrate of nitric acid is a colorless (if nitrous acid is present, a yellowish red), caustic, volatile, acid liquid, which very readily gives up three fifths of its nitrogen, whilst it evolves usually nitric oxide, NO_2, which forms yellowish red vapors in the air. It converts all the metals (excepting platinum, iridium, rhodium, and gold), and most of the lower metallic oxides, into the higher oxides; it oxidizes all the sulphides, excepting that of mercury, into sulphates, usually with the deposition of sulphur, which becomes, by long digestion, sulphuric acid. It forms soluble salts with all the metallic oxides, on which account it dissolves all these oxides, and cannot be precipitated by any reagent. Only the binoxide of tin and teroxide of antimony, in part also tellurious and tungstic acid, are insoluble in nitric acid on the oxidation of their metals; also the sulphate of lead produced by nitric acid from the sulphide; many of the nitrates are more difficultly soluble in nitric acid than in water; the basic nitrates which are insoluble in water are readily dissolved in dilute nitric acid, or the other mineral acids.

Nitric acid (or the nitrates) when warmed along with concentrated chlorhydric acid, results in the formation of chlorine (or a chloride), hypochlornitric acid NO_2Cl_2, and water ($NO_5 + 3HCl = Cl + NO_2Cl_2 + 3HO$); gold leaf is immediately dissolved in this solution, and tincture of indigo decolorized.

If a solution of nitric acid, or of a nitrate, be mixed with a larger volume of pure concentrated sulphuric acid, and, after it has become cool, there be poured on this fluid a layer of a concentrated solution of protosulphate of iron, there will be seen at the plane of contact, according to the quantity of nitric acid present, a violet, amethystine-red, or even a blackish-brown color, which increases on careful agitation of the vessel, but disappears on heating. In the absence of compounds of chlorine, the smallest traces of nitric acid can be detected in this way. Very dilute solutions (as for example mineral, rain, and spring waters, or the watery extracts of soils) must be properly concentrated before the application of this reaction. If a fluid containing nitric acid is warmed along with sulphuric acid and a drop of tincture of indigo, the blue color of the latter is converted into a yellow; this reaction is made more delicate by the addition of some chloride of sodium.

If a dry and *pure* nitrate be heated along with concentrated sulphuric acid, *colorless* fumes of the hydrate of nitric acid will be evolved, which will produce a white cloud with ammonia, and will not make a solution of silver turbid.

In the presence of some metallic *copper* or *protosulphate of iron*, or on fusion of a nitrate with bisulphate of potassa, reddish-brown vapors of nitrous acid are evolved, and also chlorine gas, if any compound of chlorine is present. All the nitrates evolve ammonia, if fused with hydrate of potassa, and an organic substance free from nitrogen, as sugar.

All the nitrates are decomposed at a high temperature; and under such exposure the nitrate of ammonia furnishes nitrous oxide and water, the rest according to the nature of the base oxygen, and a lower grade of oxidation of the nitrogen. When heated with charcoal, and especially with cyanide of potassium, phosphorus, or sulphur, they detonate very violently.

b. HYPONITRIC ACID, NO_4, and NITROUS ACID, NO_3.—These are yellowish-brown or reddish-brown gases, formed when nitric oxide comes into contact with oxygen, and also by heating many of the nitrates; when agitated with water they become colorless, nitric acid and nitric oxide being formed, and when exposed to intense cold, they are condensed to brown or bluish-green liquids. They are constituents of the red, fuming nitric acid. Their salts are mostly soluble in water.

The aqueous solutions of the alkaline nitrites are decomposed by *sulphydric acid*, with the formation of sulphides, and the acids also, with the precipitation of sulphur. These acids, with dilute sulphuric or nitric acid, soon develop yellowish-red fumes; they decolorize upon the addition of these acids the permanganate of potassa (detection of nitrous acid in nitric acid), and chromate of potassa gradually becomes a greenish-blue. All the neutral nitrites color the protosalts of iron a blackish-brown (distinguishing them from the nitrates).

They reduce the *terchloride of gold* to a brown, and the *subsalts of mercury* to a gray metal.

The protosalts of cobalt gradually occasion a yellow precipitate with the alkaline nitrites; the protosalts of nickel are not precipitated.

Nitrite of ammonia, or the nitrites along with chloride of ammonium, yield nitrogen and water, when their aqueous solution is heated $(NO_3 + NH_3 = 2N + 3HO)$; Urea is immediately decomposed by nitrous acid (not by nitric) with the evolution of carbonic acid and nitrogen $(C_2H_4N_2O_2 + 2NO_3 = 2CO_2 + 4N + 4HO)$.

Many nitrogenous compounds (so-called protein substances) are colored intensely red when warmed with a solution of mercury containing a nitrite, in nitric acid.

c. Nitric Oxide, NO_2.—This is a colorless gas, which becomes reddish brown on contact with oxygen, with the formation of nitrous and hyponitric acid. It is immediately absorbed by a solution of the protosalts of iron, conferring a reddish or blackish-brown color, and by concentrated nitric acid, with a blue, green, or yellow color, by which peculiarities it is distinguished from all the known gases. The first compound contains one equivalent of nitric oxide for four equivalents of the protosalts of iron; on its formation depends the surest method for the detection of nitric acid. Nitric oxide, like all the oxides of nitrogen, yields its oxygen to ignited metallic copper, whilst the nitrogen is set free.

d. Nitrous Oxide, NO.—A colorless gas, (unchanged by contact with oxygen, and somewhat soluble in water,) in which a glowing spark is kindled, as in oxygen gas. It is distinguished from the latter, by the fact that it can be mixed with nitric oxide without a change of color. Warmed potassium removes all the oxygen from the nitrous or nitric oxide; with the former the original volume is not changed by this removal, with the latter it is diminished one half.

Nitrogen is a permanent, colorless gas, neither changed nor absorbed by any agent. Burning bodies are extinguished in it. For the detection of nitrogen as a constituent of organic compounds, the dry compound is fused along with hydrate of potassa, by which means *ammonia* is evolved; or it is heated along with some *potassium* in a small test tube, and the aqueous solution is tested, by means of a protosalt of iron and chlorhydric acid, or by sulphide of ammonium and the sesquichloride of iron, for *cyanogen* (which see).

4. Acids of Chlorine.

a. Chlorhydric Acid (*Muriatic acid*), HCl, and the Chlorides. — Chlorhydric acid is a very fuming, acid gas with a suffocating odor, which is freely absorbed by water, forming the hydrate; on boiling the concentrated aqueous solution, a portion of the gas escapes, and the dilute acid remains behind. Chlorhydric acid, with all the basic metallic oxides forms metallic chlorides and water; with the higher oxides (also with the chromates, chlorates, hypochlorites, etc.) it disengages *chlorine*, particularly on being heated; with nitric acid, chlorine and hyporchlornitric acid (aqua-regia). The pure acid does not destroy (bleach) vegetable colors. Its solution comports itself with reagents like solutions of the chlorides.

Some of the latter are buttery or fluid and volatile (chloride of antimony, of tin, and of arsenic), some solid, fusible, and non-destructible by fire (chloride of silver, lead, potassium, sodium, barium, etc.), some decomposable into chlorine and the metal (chloride of gold, and of platinum), or, on the admission of air, into chlorine and a metallic oxide (the chloride of iron, etc.). Nearly all the chlorides are soluble in water; the chloride of silver, $AgCl$, and the subchloride of mercury, Hg_2Cl, are *insoluble*; the subchloride of copper, Cu_2Cl, the protochloride of gold, $AuCl$, and the protochloride of platinum, $PtCl$, are nearly insoluble; the protochloride of lead, $PbCl$, and some oxychlorides are *with difficulty* soluble.

The aqueous solutions of the chlorides give, with *nitrate of silver*, a white, curdy precipitate of the chloride of silver, $AgCl$, (see page 57,) becoming violet in the light; this is insoluble in dilute nitric acid, very readily soluble in ammonia. If there is great dilution, there will be produced an opalescent turbidness.

A white precipitate of the subchloride of mercury, Hg_2Cl, (see page 59,) is occasioned by the *subnitrate of mercury*, which is insoluble in water and in dilute acids, though very soluble in chlorine water.

Acetate of lead precipitates in moderately dilute solutions the white chloride of lead, $PbCl$, (see page 54,) soluble in much water.

When heated with sulphuric acid, the chlorides disengage chlorhydric acid gas ($NaCl + SO_3, HO = NaO, SO_3 + HCl$). The chlorides of mercury, silver, lead, and tin, are either not decomposed by sulphuric acid, or only so with difficulty. The chlorides yield the yellowish-green *chlorine* gas, along with the binoxide of manganese and sulphuric acid, (see page 40,) and, on the other hand, along with dry chromate of potassa and sulphuric acid, brownish-red fumes of *chlor-chromic acid*, $CrOCl$, (see page 25,) which ammonia dissolves with a yellow color (a mode of distinguishing the chlorides from the bromides and iodides).

Before the blowpipe the chlorides impart a blue color to flame if they are heated along with a pearl of phosphate of ammonia-soda, which has been saturated with the protoxide of copper.

b. Perchloric Acid, ClO_7.—This is formed at the commencement of the decomposition of chlorate of potassa by high temperature, or by sulphuric acid. The aqueous solutions of perchloric acid, or its salts, do not bleach vegetable colors. The perchlorates are completely soluble in water; and *the salts of potassa* produce in moderately dilute solutions a crystalline precipitate, (KO, ClO_7), which is quite insoluble in alcohol.

The perchlorates of the alkalies and alkaline earths are resolved at a red heat into oxygen gas and chlorides; they detonate slightly on charcoal. They are only with difficulty decomposed (without the formation of bleaching liquids) on being heated along with concentrated sulphuric acid, and are not at all decomposed by dilute acids. By this reaction they are easily distinguished from the salts of the following acids.

c. Chloric Acid, ClO_5.—This is formed by the action of chlorine on aqueous solutions of alkaline oxides at a high temperature ($6\,KO + 6\,Cl = 5\,KCl + KO, ClO_5$). Hydrated chloric acid is a colorless liquid, which first reddens litmus, and then bleaches it, and which is resolved, on being heated, into perchloric acid, oxygen, and chlorine. It is readily deoxidized by sulphydric, sulphurous, and phosphorus acid, chlorhydric acid, and many organic compounds.

The chlorates are entirely soluble in water, and on this account they cannot be precipitated by any metallic oxide (nor by the nitrate of silver). Their aqueous solutions *do not bleach.* On being heated by themselves, they fuse and disengage oxygen, or a mixture of chlorine and oxygen, whilst the chloride, or with some the oxide or basic chloride, remains behind. With combustible bodies (phosphorus, sulphur, charcoal, sugar, etc.), they detonate very powerfully, on the application of heat, violent friction, or by contact with fuming sulphuric acid.

If a small portion of a chlorate and some phosphorus are brought into contact with sulphuric acid under water, the phosphorus is inflamed. Concentrated sulphuric acid, in contact with the chlorates, is colored first brown or yellow, whilst a very explosive, greenish-yellow gas, ClO_4, escapes. $3\,(KO,\ ClO_5) + 4\,SO_3 = 2\,(KO,\ 2\,SO_3) + KO,\ ClO_7 + 2\,ClO_4)$. If chlorate of potassa is warmed along with chlorhydric acid, the liquid becomes yellow, with the abundant disengagement of chlorine, and of an acid resembling the hypochloric. ($3\,(KO,\ ClO_5) + 5\,HCl = 3\,KCl + Cl_3O_{13} + Cl_2 + HO$.) This mixture serves as a powerful oxidizing agent and solvent.

d. HYPOCHLORIC ACID, ClO_4.—A greenish-yellow gas, smelling like nitrous acid and burnt sugar, readily detonating, resolved along with bases into a chlorate and chlorite. It bleaches like free chlorine. See chloric acid, for its formation.

e. CHLOROUS ACID, ClO_3.—Produced by the action of nitrous acid (or nitric acid in the presence of arsenious or tartaric acid) on the chlorate of potassa. It is a yellowish-green gas, easily decomposed, and acting like chlorine. It decolorizes the permanganate of potassa. The chlorites are readily resolved into chlorides and chlorates; their solutions give pale yellow precipitates with the nitrate of lead and of silver.

f. Hypochlorous Acid, ClO. — Produced, along with a chloride, by the action of chlorine on the protoxide of mercury, or excess of alkaline oxides, in the presence of water, at a low temperature ($2\,CaO + 2\,Cl = CaO, ClO + CaCl$). It is a reddish-yellow gas, converted easily with detonation into chlorine and oxygen, — is quite soluble in water. Its odor and properties are similar to chlorine.

The hypochlorites (bleaching salts) are always mixed with the chlorides; bleaching-lime contains also some of the hydrate. They are all soluble in water, possessing a caustic taste, a peculiar chlorine-like odor, and their aqueous solution (still better on the addition of an acid) bleaches and oxidizes powerfully. They are resolved by heat into chlorides and chlorates; even with very dilute acids, the bleaching salts, (which are mixed with the chlorides), disengage chlorine ($CaCl + CaO, ClO + 2\,SO_3 = 2\,(CaO, SO_3) + 2\,Cl$), the pure salts, under like circumstances, evolve hypochlorous acid.

The hypochlorites of the alkalies precipitate gradually, from the *protosalts of manganese*, the brown binoxide, from the *protosalts of lead*, at first the chloride, and afterwards the binoxide, from the *salts of silver* the chloride, from the *subsalts of mercury* the subchloride.

If a solution of arsenious acid in chlorhydric acid, colored blue by the solution of indigo, is gradually mixed with a dissolved bleaching salt, then will the chlorine decolorize the liquid only when all the arsenious acid has been converted into arsenic acid. (On this rests the estimation of the value of bleaching powder by the employment of solutions of arsenious acid and bleaching powder of a determined value.)

Chlorine is, at ordinary temperatures, a pale greenish-yellow gas, of a suffocating odor. *Chlorine water* is pale yellow, smells and acts like chlorine, bleaches litmus and indigo immediately, and gives, with *sulphydric acid*, a precipitate of sulphur; with *nitrate of silver*, a precipitate of chloride of silver; with *acetate of lead*, the chloride and binoxide of lead. It dissolves gold leaf with ease. Shaken with metallic mercury, it forms the subchloride, whilst all the free chlorine disappears; if it contain chlorhydric acid, the supernatant liquid will be acid and will produce chloride of silver if nitrate of silver is added. Shaken with excess of subchloride of mercury, pure chlorine water furnishes an acid solution of the protochloride of mercury, which becomes neutral on the addition of chloride of sodium; in the presence of chlorhydric acid this remains *acid*, and if hypochlorous acid is present, it *bleaches*, since the latter does not dissolve the subchloride of mercury. Very small quantities of free chlorine (ex. gr. in chlorhydric acid) can be detected by a mixture of starch and iodide of potassium, which becomes blue; large quantities of chlorine destroy the blue color again.

The *perchlorates* and *chlorates* are easily recognized, since they do not bleach, are not precipitated by the heavy metallic oxides, and — if the base is an alkali, or an alkaline earth — leave behind, on ignition, a *neutral* residuum, which comports itself as a metallic chloride. The *nitrates* of the same bases yield an alkaline residuum; they also give off red nitrous acid fumes, when mixed with sulphuric acid and copper filings; these fumes are absorbed by protosulphate of iron, giving it a brown color.

The *hypochlorites*, either by themselves, or on the addition of the weakest acids, destroy vegetable colors; the *chlorides* with concentrated sulphuric acid disengage pure chlorhydric acid gas, which reddens litmus, but does not bleach. Chlorhydric acid gas, or chlorine produces in a drop of nitrate of silver, hanging to a glass rod, the white, curdy chloride of silver, which speedily disappears in ammonia.

5. Acids of Bromine.

a. Bromhydric Acid, HBr, and Bromides. — The compounds of bromine comport themselves very like the corresponding compounds of chlorine. Bromhydric acid, or solutions of the bromides, gives with *nitrate of silver*, a yellowish-white, curdy precipitate, $AgBr$, insoluble in nitric acid, with difficulty soluble in ammonia, and very soluble in cyanide of potassium, and in hyposulphite of soda.

Subnitrate of mercury throws down the yellowish-white sub-bromide of mercury, Hg_2Br, insoluble in dilute nitric acid, very soluble in chlorine water, giving a yellowish-brown color to the liquid.

Acetate of lead throws down the white bromide of lead, $PbBr$, soluble in water with great difficulty, though very soluble in nitric acid.

The bromides, when warmed with concentrated nitric acid, yield brownish-red vapors of bromine, with concentrated sulphuric acid, bromhydric acid, and at the same time free bromine and sulphurous acid ; and on the addition of the binoxide of manganese, only bromine, which will color any starch paste that may be present in the upper portion of the test tube, a fiery yellow. Sulphuric acid containing hyponitric acid (or nitrite of potassa and chlorhydric acid) will *not separate* bromine from the bromides.

All the bromides are decomposed by free chlorine, with the formation of a chloride and the separation of the bromine. If a solution of a bromide, even of a permanent bromide, as the bromide of silver, is mixed with chlorine water, the fluid will be colored yellow by the separated bromine. Ether dissolves, on agitation with it, all the bromine with a yellow or brownish-yellow color. (By the intensity of this color, the quantity of bromine can be judged, by comparing it with a solution containing a known quantity.) The ethereal solution of bromine with a loss of its color, gives up to potassa-lye all its bromine, as a bromate of potassa and a bromide of potassium, and the alkaline fluid, when saturated with sulphuric acid, again yields the vapors of bromine on redistillation. (Determination of bromine in the mother-lye of mineral springs. In case of very small quantities of a bromide, there should be digestion with alcohol, and the insoluble salt, after the evaporation of the alcohol, should be treated as above.)

A bead of phosphate of ammonia-soda saturated with protoxide of copper, colors, on the addition of a bromide, the flame of the blowpipe a greenish-blue.

b. BROMIC ACID, $Br\,O_5$. — This acid comports itself like chloric acid. Its salts, on ignition, evolve oxygen (in a part along with bromine) and are converted into bromides.

Warmed with *sulphuric acid*, they yield oxygen, and brownish-red *vapors of bromine;* with concentrated chlorhydric acid, chloride of bromine, with a yellow coloring.

The soluble bromates are precipitated white, in moderately dilute solutions, by the *protosalts of lead,* white by the *protosalts of silver,* readily soluble in ammonia though with difficulty soluble in nitric acid; they are precipitated a clear yellow by the *subnitrate of mercury.*

Bromine is a dark, brownish-red, heavy liquid, emitting suffocating yellowish, or brownish-red vapors; its yellow or red aqueous solution decolorizes litmus and indigo, gives with sulphydric acid a precipitate of sulphur, with starch a fiery yellow precipitate, and comports itself in general like chlorine water.

The bromides are specially characterized by their comportment towards sulphuric acid and chlorine, and hence are easily distinguished from the chlorides. The bromide of silver, along with the first portions of the chloride of silver, is thrown down from the mother-lye, by fractional precipitation with the nitrate of silver.

6. Acids of Iodine.

a. Iodhydric Acid, HI, and the Iodides. — These are similar in their reactions to the corresponding compounds of chlorine and bromine.

Iodhydric acid, as also those iodides which are soluble in water, is precipitated yellowish white (AgI), by the *nitrate of silver*, even in very dilute solutions, — the precipitate is insoluble in nitric acid, and in ammonia; by the *subnitrate of mercury* a greenish-yellow precipitate (Hg_2I) is produced, insoluble in dilute nitric acid, though soluble in iodide of potassium; by the *protosalts of mercury* a scarlet red (HgI), insoluble in dilute nitric acid, soluble in iodide of potassium, and in the precipitant; by the *protosalts of lead*, an orange yellow (PbI), soluble in dilute nitric acid; by the *protochloride of palladium*, a black (PdI), insoluble in chlorhydric acid, soluble in ammonia, — this precipitation takes place gradually, when there is great dilution, and serves to separate iodine from chlorine and bromine; by *protosulphate of copper*, a dirty white (Cu_2I), — the precipitate being complete in the presence of sulphurous acid, or the protosalts of iron.

The iodides are readily decomposed, either in aqueous solution or in the dry condition, by *chlorine* or *bromine* in gaseous form, or in aqueous solution; by concentrated *nitric acid*, nitrous and hyponitric acid (or their combination with sulphuric acid), by the *binoxide of barium*, and *chlorhydric acid*, by concentrated *sulphuric acid*, or *sulphuric acid* and the *binoxide of manganese*, with *the separation of the iodine*, which, according to the quantity or the nature of the iodide, is either precipitated as a black powder, or remains in solution with a brownish-yellow color, or is volatilized as a characteristic violet vapor.

If free iodine, separated from any combination, comes into contact with *starch-paste*, there is produced a blue compound (in very small quantities of iodine, a violet or rose-red, and in excess of iodine a green), on the formation of which, the most delicate detection of iodine rests. In searching for very small quantities of iodine, the fluid to be tested (either neutral or slightly alkaline) is mixed with some drops of clear, thin starch-paste, and then by means of a glass rod sulphuric acid, containing a trace of hyponitric acid (sulphate of nitric oxide or a mixture of fuming red nitric acid and sulphuric acid), is added; or nitrite of potassa is added to the fluid which has been made acid by chlorhydric acid. If the smallest trace of iodine is present, the fluid acquires a bluish or reddish color.

By shaking those liquids, from which the iodine has been separated by the above reagents (if starch is not mixed with them), with a few drops of the bisulphide of carbon, after settling, the smallest trace of iodine produces a violet color.

Since the blue iodide of starch is decolorized by excess of chlorine (on account of the formation of the chloride of iodine), it is necessary in the detection of very small quantities of iodine by means of chlorine, that the latter should be carefully added as dilute chlorine water, or that some of the gas be allowed to operate (furnished from an open flask containing chlorine water) on the surface of the solution to be tested.

Mother-liquor which is very poor in iodides is evaporated to dryness, treated with alcohol (for the extraction of the compound of iodine soluble in it) and then the dry residuum of the alcoholic solution is used for testing.

Dry iodides are drenched with some concentrated sulphuric acid in a stoppered flask, a strip of paper or linen covered with starch-paste is placed between the neck and stopper and allowed to stand for some hours, when, if there is even a very small quantity of iodine present, a blue color will be produced.

The blue color of the iodide of starch is immediately destroyed by alkalies, by sulphydric acid, sulphurous and arsenious acid, protochloride of tin, chloride of mercury or the active reducing, organic substances. Dilute acids, even acetic acid (but not chlorine water) bring back the blue color of the iodide of starch, which has been decolorized by alkalies. Even heating the iodide of starch, diffused in water, renders it colorless, though it becomes blue again on cooling.

The addition of an iodide to a pearl of phosphate of ammonia-soda, saturated with protoxide of copper, colors the flame of the blowpipe green.

b. Periodic Acid, IO_7. — This is produced by the action of chlorine on an alkaline solution of the iodate of soda ($NaO, IO_5 + 3 NaO + 2 Cl = 2 NaO, IO_7 + 2 NaCl$). It is crystallizable, and yields, when heated, oxygen, and violet-colored vapors of iodine.

Its soluble salts give a white precipitate with the *pro-*

tosalts of baryta, lime, and *lead,* and a brown with the *salts of silver.* All these precipitates are readily soluble in dilute nitric acid.

The dry salts comport themselves on the application of heat like the iodates.

c. IODIC ACID, IO_5.—Produced by dissolving iodine in alkaline oxides ($6KO + 6I = 5KI + KO, IO_5$), by the action of concentrated nitric acid on iodine, or by carbonate of soda on the chloride of iodine. It is crystallizable and very soluble in water. It is instantaneously reduced by sulphurous acid, nitric oxide, sulphydric acid and iodhydric acid, with the separation of the iodine, as the starch test will indicate.

Only the iodates of the alkalies are soluble in water; on ignition, they yield oxygen, or oxygen and vapors of iodine, and a residuum of an iodide. They give white precipitates with the *protosalts of baryta and lead, the subsalts of mercury,* and *the protosalts of silver; the iodate of silver* is with much difficulty soluble in nitric acid, but soluble in ammonia, whence it is precipitated, by sulphurous acid, as the *iodide of silver.*

Sulphydric acid resolves the soluble iodates into an iodide, sulphur, and some sulphuric acid; sulphurous acid separates the iodine, which is soluble in excess of the reagent; chlorhydric acid produces the chloride of iodine; solution of indigo is decolorized if added along with sulphuric acid.

A solution of an iodate in iodide of potassium is decomposed by every acid, even acetic acid, the iodine being separated, which colors starch-paste blue. (Recognition of iodic acid in iodide of potassium.) The iodates, with concentrated sulphuric acid, yield vapors of iodine, and color starch-paste, if an effective reducing agent (as the protosulphate of iron) is present. Heated on charcoal they detonate but slightly.

Iodine is of a grayish-black color, with a metallic lustre, an unpleasant odor like that of chlorine, and forms quickly, at a moderate heat, violet vapors. It colors the skin brown, which color, however, is soon dissipated. It is hardly soluble in water, readily so in alcohol, ether, iodide of potassium, and in iodhydric acid, making brown solutions, — in bisulphide of carbon, it imparts a splendid violet color, which is so intense that it serves as a delicate test for iodine. Iodine is also soluble in chloroform,* benzol, and naphtha, giving a red color. It is soluble in hyposulphite of soda, with the formation of tetrathionic acid; with sulphurous acid it produces sulphuric acid, and with sulphydric there is produced iodhydric acid, with the separation of the sulphur.

For the detection of the bromides in the presence of the iodides, the iodine is first removed by sulphuric acid containing some hyponitric acid, and continuous agitation with ether, then the judicious addition of chlorine water separates the bromine, to be recognized by the color imparted to ether shaken with it.

In the quantitative separation of iodine, bromine, and chlorine in soluble compounds, the iodine is first precipitated by the protonitrate of palladium † and the black

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* *Chloroform* is proposed as a test for iodine by Rabourdin, who says that the presence of the latter may be shown in a liquid with less than $\frac{1}{100000}$ of its weight. 150 grains of the liquid to be tested are mixed with two drops of nitric, and fifteen to twenty drops of sulphuric acid, and fifteen grains of chloroform. On shaking the mixture a violet tint is produced. The presence of bromine it is said hides the reaction, — and the presence of asulphuret produces a like effect.

TRANS.

† Where the chloride of palladium can be employed, which this particular case necessarily prevents, the $\frac{2}{1000000}$ of iodide of potassium can be detected in a quart of water. L. H. S.

precipitate, PdI, after twelve hours standing, is placed on a weighed filter; (or it is precipitated, although less exactly, by a solution of protosulphate of copper in sulphurous acid, as the subiodide of copper, Cu_2I, which is dried at 120° C). The bromine is separated from the fluid (which has been freed by sulphydric acid from excess of palladium, and then from sulphydric acid by sesquisulphate of iron free from chlorine) together with a part of the chlorine, by fractional precipitation with the nitrate of silver, the weighed precipitate is fused in a stream of chlorine gas, and the bromine calculated from the difference of weight. Or the weighed bromide and chloride of silver are decomposed by pure zinc with the addition of some drops of chlorhydric acid and the metallic silver is weighed after its complete reduction. The remainder of the chlorine is completely precipitated by nitrate of silver and weighed as AgCl.

Small quantities of chlorides in the presence of much of the bromides are most surely detected, if the dry compound, mixed with some chromate of potassa, is warmed along with concentrated sulphuric acid, and the vapors, which are then evolved, are caught in ammonia. This is colored yellow, if a compound of chlorine be present, in so far as it has produced the chromate of ammonia; it remains colorless if the compound only contains bromides. Small quantities of the chlorides cannot be detected in this way in the iodides. In this case it is best to precipitate all the iodine and chlorine by means of nitrate of silver, and then treat the precipitate with ammonia, which dissolves the chloride of silver to be recognized by the white, curdy precipitate it produces on saturation with nitric acid. A solution of chloride of silver in ammonia gives no precipitate with a chloride, but a precipitate of the iodide of silver when an iodide is employed.

Insoluble compounds, as many of an organic nature, whose solutions cannot be decomposed by nitrate of silver, are ignited (for the detection of chlorine, bromine, or iodine) with an alkaline carbonate (free from chlorine) or caustic lime, and the aqueous solution of the ignited mass, after it has been saturated with dilute nitric acid, is tested by nitrate of silver.

7. ACIDS OF CYANOGEN.

a. CYANHYDRIC ACID (PRUSSIC ACID) HCy and THE CYANIDES. — Cyanhydric acid is a liquid as clear as water, inflammable, and very volatile, of a peculiar stupefying odor; it mixes in every proportion with water, alcohol, and ether, and is readily decomposed when pure. Along with alkalies and concentrated acids it is resolved into formic acid and ammonia ($C_2NH + 3HO = C_2HO_3 + NH_3$).

The cyanides of the alkalies and the alkaline earths are readily soluble in water; their solutions have an alkaline reaction, smell strongly of cyanhydric acid, and are decomposed by every dilute acid with the disengagement of cyanhydric acid. The protocyanides of the heavy metals are mostly insoluble in water (the protocyanide of mercury is an exception) and are not decomposable by *oxygen acids,* though *chlorhydric acid* or *sulphydric acid* effect this decomposition, with the separation of cyanhydric acid. The cyanide of potassium and of sodium, on ignition, remain unchanged, if kept free from contact of the air, or if the air is present, they are converted into cyanates; the protocyanides of the heavy metals (as that of mercury), yield cyanogen gas and the metal; the rest are resolved into nitrogen and a carbide or paracyanide of the metal.

The cyanides of the alkalies form along with many other cyanides, soluble double cyanides. Thus the cyanides of *gold*, *palladium*, *silver*, *copper*, *cadmium*, *nickel*, *cobalt*, *iron*, and *zinc*, are very soluble in cyanide of potassium; the solution is again precipitated by the caustic or carbonated alkalies. In some of these alkaline double-cyanides, as those of *silver*, *mercury*, and *cadmium*, the heavy metal is precipitated, by sulphydric acid, as a sulphide, in others this precipitate is not produced, as in those of *iron* and *cobalt*, or only partially and with difficulty effected, as in those of *manganese*, *nickel*, *zinc*, and *copper*.

Nitrate of silver throws down, in aqueous solutions of cyanhydric acid, or of cyanide of potassium, the white, curdy cyanide of silver, $AgCy$,—insoluble in dilute nitric acid, soluble in hyposulphite of soda, in ammonia, cyanide of potassium, and concentrated nitric acid. With concentrated chlorhydric acid it evolves the odor of cyanhydric acid, by which reaction it is readily distinguished from the chloride, bromide, or iodide of silver; on ignition, it is resolved into cyanogen gas, and half-cyanide of silver, or the metal.

Subnitrate of mercury precipitates the gray reduced mercury; the fluid then contains the cyanide of mercury ($CyH + Hg_2O = HgCy + Hg + HO$).

Cyanide of potassium, or cyanhydric acid, precipitates the white subcyanide of copper, Cu_2Cy, from a solution of *protosulphate of copper* mixed with sulphurous acid, which is soluble in cyanide of potassium; the cyanide of potassium precipitates the hydrated sesquioxide of iron, from the *sesquichloride of iron*, with the disengagement of cyanhydric acid.

The protosalts of iron give, with cyanide of potassium (though not with free cyanhydric acid) a yellowish-red precipitate (Fe Cy?),—soluble in much cyanide of potassium, especially on the addition of potassa; the fluid then contains *the ferrocyanide of potassium.* On this reaction depends one method for the detection of cyanhydric acid: the liquid to be tested is first mixed with potassa, then with a proto-sesquisalt of iron (a solution of the sulphate of iron exposed to the air), and finally with excess of chlorhydric acid, which dissolves all the proto- and sesquioxide of iron that were precipitated, while the pure Prussian blue is left behind; if there are only traces of cyanhydric acid present, then there will be formed a bluish-green fluid, from which blue flakes are gradually deposited.

The following treatment is still more delicate. The liquid mixed with some yellow sulphide of ammonium (if only traces of cyanhydric acid are suspected, one drop will answer), and heated until it becomes colorless. Now if cyanhydric acid is present, sulphocyanide of ammonium is formed, which produces a blood-red color with the sesquichloride of iron. In judicial investigations for cyanhydric acid (small quantities are readily recognized by their odor), the aqueous distillate obtained by dint of good refrigeration is treated in this way, after it has been determined whether the substance to be tested does not produce immediately, with the sesquisalts of iron, the Prussian blue, which fact would show the presence of (the non-poisonous) ferrocyanide of potassium. Before the distillation some tartaric or phosphoric acid is added to the fluid, if it is not already acid.

A liquid containing cyanhydric acid dissolves the *protoxide of mercury*, converting it into the protocyanide, which is not precipitated by alkalies; sulphydric acid precipitates the protosulphide of mercury from the alkaline liquid, by which means likewise small quantities of cyanhydric acid can be recognized. If the liquid, treated with the protoxide of mercury, contain at the same time free chlorhydric acid, then ammonia throws down *the white precipitate.*

If cyanhydric acid, containing chlorhydric acid, be evaporated along with borax to dryness, only the cyanhydric acid is driven off; the chlorhydric acid can be determined in the residuum by nitrate of silver.

Heated along with concentrated sulphuric acid, the cyanides are resolved into the sulphate of the metallic oxide, ammonia, and carbonic oxide. ($C_2NM + 4(SO_3, HO) = MO, 2SO_3 + NH_4O, 2SO_3 + 2CO$). All the compounds of cyanogen, when ignited along with protoxide of copper, yield one volume of nitrogen for two volumes of carbonic acid.

All the soluble as well as insoluble double cyanides, which are otherwise difficult to decompose, are easily and perfectly decomposed by heating them along with three to four parts of a mixture, of three parts of sulphate of ammonia, and one of nitrate of ammonia, which constitutes an excellent method for recognizing and determining the metals that are left behind as sulphates.

Cyanogen, C_2N, is a colorless, coercible gas, of a peculiar odor, which is very irritating to the nose and eyes. It burns with a bluish violet flame. It is somewhat soluble in water, and abundantly so in alcohol; these solutions speedily decompose, becoming brown, and then they contain carbonic acid (oxalic acid), ammonia, urea, and paracyanogen. Cyanogen gas is completely absorbed by hydrate of potassa, as well as by moist protoxide of mercury, though in the latter case slowly.

b. Cyanic Acid, Cy O. — The cyanates are easily recognized, since when mixed with the stronger acids, effervescence is induced, and they evolve carbonic acid, which possesses the penetrating odor of the undecomposed volatilized cyanic acid. The solution contains a salt of ammonia. The alkaline cyanates are not decomposed by ignition; their aqueous solutions are decomposed when heated, carbonic acid and ammonia being formed. ($C_2NO + 3HO = NH_3 + 2CO_2$.)

The cyanates give a white precipitate with the *protonitrate of silver and of lead*, and *the subnitrate of mercury*; a greenish brown with *the protonitrate of copper*, a brownish yellow with *the terchloride of gold*. Evaporated along with sulphate of ammonia, urea is formed.

The salts of *fulminic acid*, Cy_2O_2, explode very easily by heating, percussion, or even by contact with concentrated sulphuric acid.

The salts of *cyanuric acid*, Cy_3O_3, with an alkaline base, are separated by heat into hydrated cyanic acid, cyanate of ammonia, carbonic acid, and nitrogen, and a cyanate is left as the residuum.

c. Sulphcyanhydric Acid, (Sulphoprussic Acid) H, CyS_2. — Found in saliva. The sulphcyanides are mostly soluble in water and also in alcohol.

They give white precipitates with a mixture of *protosulphate of copper* and *sulphurous acid*, with *the subsalts of mercury*, *the protosalts of silver*, and *the salts of teroxide of gold*. The sulphcyanide of silver (CyS_2, Ag) is insoluble in dilute nitric acid, and serves for the determination of sulphcyanhydric acid in soluble compounds.

The sulphcyanides acquire a blood-red color along with *the sesquichloride of iron*, or in very great dilution a reddish-yellow color, which can be distinguished from similar colors, as it does not become pale yellow on the addition of much chlorhydric acid, and it evolves, with zinc, sulphydric acid. Most of the sulphcyanides are resolved, on ignition, into nitrogen, cyanogen, bisulphide of carbon, and a metallic sulphide. ($4\,C_2NS_2, M = N + 3\,C_2N + 2\,CS_2 + 4\,MS$.)

d. FERROCYANHYDRIC ACID, $Fe\,Cy_3 + 2\,H = Cfy, H_2$; FERRICYANHYDRIC ACID, $Fe_2Cy_6 + 3\,H = 2\,Cfy, H_3$, and ANALOGOUS COMPOUNDS.

The *ferrocyanides* of the alkalies are soluble in water, colorless when anhydrous, but yellow as hydrates. Most of the other ferrocyanides are insoluble in water, many also in acids; some are white — as those of the earths, of zinc, lead, silver, and mercury; — others are remarkable for lively colors, on which account *the ferrocyanide of potassium* ($Cfy, 2\,K$) is employed for the recognition of many metallic salts, but especially for those of *iron* and *copper*.

The sesquisalts of iron produce a blue precipitate, $3\,Cfy, 4\,\dot{F}e$, with the soluble ferrocyanides (vide page 45); *protosalts of iron* a white, or bluish white, $2\,Cfy, Fe_3, K$, (vide page 43); *protosalts of copper* a brownish red, $Cfy, 2\,Cu$, (vide page 65).

The *ferricyanides* of the alkalies are yellowish red; they are essentially different from the ferrocyanides, since their aqueous solutions give immediately a blue precipitate, $2\,Cfy, 3\,Fe$, (vide page 43), with *the protosalts of iron*, and none with *the sesquisalts of iron*, but only give a darker color to the solution.

The soluble ferrocyanides and ferricyanides are decomposed, when warmed with dilute sulphuric acid, since a portion of the cyanogen is disengaged as cyanhydric acid [$2\,(2\,K\,Cy, Fe\,Cy) + 6\,(S\,O_3, H\,O) = 3\,H\,Cy + K\,Cy, 2\,Fe\,Cy + 3\,(K\,O, H\,O, 2\,S\,O_3)$]. Excess of concentrated sulphuric acid disengages carbonic oxide gas with them all (vide page 149). Caustic alkalies decompose all the insoluble ferrocyanides and ferricyanides, with the separation of the basic metallic oxide and the reformation of the ferrocyanide or ferricyanide of alkali-metal; on ignition with carbonate of potassa, the cyanide of potassium (along with the cyanate of potassa) and the reduced heavy metal are produced. By heating with sulphate of ammonia, they are readily and completely decomposed (vide page 149).

Nitro-ferricyanhydric acid ($Fe_2Cy_5NO_2, H_2$), which forms compounds very like the ferricyanides, is produced by the action of nitric acid on ferrocyanide of potassium. It is specially characterized by the fact that its soluble compounds produce, in solutions which contain even a very small quantity of a soluble sulphide, a splendid blue, or even a violet color, which is evanescent; on which account it is employed as a delicate reagent for the detection of soluble sulphides (vide page 107). The color is not produced with free sulphydric acid.

Cobalt as well as *chromium* and *manganese*, enter into combination with cyanide of potassium, as cyanides, which exhibit analogous properties with the ferricyanide of potassium. An aqueous solution of *the cobalto-cyanide of potassium*, $Co_2Cy_6, 3K$, is not decomposed by being boiled with dilute sulphuric, nitric, or chlorhydric acid, by chlorine in the presence of free alkali, or by the protoxide of mercury, while the solution of cyanide of nickel in the cyanide of potassium is decomposed under these circumstances. (Separation of nickel from cobalt).

The soluble cobalto-cyanides give a clear blue precipitate with *the protosalts of copper*, a *greenish blue* with *the protosalts of nickel*, a reddish with *the protosalts of cobalt*, and a white with *the protosalts of iron* and *the subsalts of mercury*. These precipitates are mostly insoluble in dilute acids and readily decomposed by alkalies. By being heated along with concentrated sulphuric acid, or still better with sulphate and nitrate of ammonia, the cobalto-cyanides are completely decomposed.

8. Fluohydric Acid, HF, and the Fluorides.

Fluorine is mostly found as Fluorspar (CaFl). It is a constituent in many natural compounds of phosphoric and silicic acid (Wavellite, Topaz, Cryolite, Mica, Tourmaline, Hornblend, etc.); occurs as the fluoride of calcium, in the bones and teeth, as also in the ashes of many plants, and in mineral springs.

Fluohydric acid is a very volatile liquid, fuming strongly in the air with irritating fumes, miscible with water inall proportions; its most characteristic property is that it dissolves free or combined silicic acid with ease, and consequently corrodes glass, or makes it dim, whence its application in the decomposition of the silicates, — the only sure method of recognizing fluorine depends also on this property.

In the solution of silicic acid there is produced the terfluoride of silicium, SiF_3, which unites with excess of fluohydric acid, forming the silico-fluohydric, $3HF, 2SiF_3$; in the presence of a base (with a silicate) it forms a silico-fluoride of the metal, and, according to the proportion of the base with the silicic acid, also a fluoride of the metal or the terfluoride of silicium. Boracic, tantalic, titanic, molybdic, and tungstic acid are also readily decomposed and then dissolved by fluohydric acid, with the formation of analogous compounds; gold and platinum are not affected by it, and lead only with great difficulty.

Some of the fluorides are fluid and volatile, others solid, resisting fire, and some soluble, others insoluble in water.

The soluble fluorides, with *the chloride of calcium*, give a gelatinous precipitate (CaF), which is more apparent on heating and on the addition of ammonia, and is slightly soluble in ammoniacal salts, and dilute chlorhydric or nitric acid, (with more difficulty in acetic acid).

The *protosalts of lead* give a white precipitate (PbF) soluble in nitric acid; the fluorides are not precipitated by the *nitrate of silver.*

All the fluorides are decomposed by concentrated sulphuric acid, with the development of fluohydric acid. Fluorspar forms in this way a pasty mass, not etching glass, but which on being warmed disengages the acid in gaseous form. Many insoluble fluorides (like the fluoride of calcium) are only completely decomposed by fusion when silica is present, along with an alkaline carbonate.

For the qualitative detection of fluorine (in bones, teeth, or minerals free from silicic acid), the finely pulverized substance is rubbed, along with concentrated sulphuric acid, to a pasty condition, and warmed in a large platinum crucible, after which the crucible is covered with a watch-glass, whose convex side is coated with wax, and has radii scratched through the wax so as to leave the glass exposed at some places; some water is poured in the watch-glass so that the wax does not melt. After some hours standing, the wax is taken carefully from the warmed watch-glass, when, if fluorine were present, the uncovered places of the glass will be corroded and look dim; with very small quantities of fluorine, the dim places become visible only by breathing on the well-dried glass.

If the compound to be tested for fluorine, contain also silicic acid, then it is fused with carbonate of soda-potassa, treated with water, the silica removed from the solution by some carbonate of ammonia, and being nearly neutralized with acetic acid, a precipitate is produced by chloride of calcium. The precipitate thus formed, which must contain all the fluorine, is then tested as given above. Or the finely-pulverized compound containing silicic acid is warmed in a dry glass flask, along with concentrated sulphuric acid with the addition of a small piece of marble, and the fluoride of silicium, which is then evolved (along with carbonic acid) is conducted into ammonia. The fluid is then evaporated, the residuum extracted with water, the filtrate again evaporated, and the resulting mass of salts is to be tested for fluorine, in the usual way, being mixed with sulphuric acid in a platinum crucible covered with a glass plate overspread with wax.

If a fluoride is heated, with phosphate of ammonia-soda, at the end of a glass tube open on both sides in such a way that the flame partly strikes in the tube, there is disengaged, along with aqueous vapor, fluohydric acid, which colors logwood paper a straw-yellow, and leaves a dim speck on the glass after evaporation.

Several silicates containing fluorine (Mica and Tourmaline) develop, by heating them alone, the terfluoride of silicium.

For the determination of fluorine in the presence of phosphoric acid in insoluble compounds, they are fused along with carbonate of soda-potassa and silica, the silica is precipitated from the aqueous solution by carbonate of ammonia, and then, after the most of the alkaline carbonate has been neutralized, the phosphoric acid and the fluorine by means of chloride of calcium. For the removal of the carbonate of lime contained in it, the precipitate, after its ignition, is saturated with acetic acid, evaporated in a water bath, washed out with water, ignited and weighed. By warming with concentrated sulphuric acid, the fluorine now is driven off, the sulphate of lime is precipitated by alcohol, and the phosphoric acid, in the filtrate, as the phosphate of ammonia-magnesia.

9. [BORACIC ACID, BoO_3.]

Sometimes found free (*Sassolin*), sometimes united with bases in Tincal, Boracite, Dathilite, also in smaller quantities in Tourmalines, in Axinite, Apyrite, Rhodizite, etc., and in mineral springs.

Boracic acid forms (when a hydrate) scaly crystals, or (when anhydrous) a vitreous mass, perfectly resisting fire. It is soluble in water and in alcohol; and these solutions turn tumeric paper, dipped in them, brown when dry. On evaporating these solutions a part of the boracic acid is always volatilized along with the vapors of the solvent; this volatilization is not prevented by ammonia, ammoniacal salts or the protoxide of lead, though prevented by excess of carbonate of soda; on evaporation and ignition along with the chloride of ammonium boracic acid is partly changed into the infusible boride of nitrogen. The alcohol solution of boracic acid burns with a *green* flame, on which peculiarity rests the surest mode for its detection.

The alkaline borates are readily soluble in water, with an alkaline reaction; their aqueous solutions absorb carbonic acid, sulphurous acid, sulphydric acid and chlorine in large quantities. They also dissolve sulphur, arsenious acid, and the fat acids in large quantity. By evaporating an alkaline borate along with chlorhydric acid, the alkaline metallic oxide is converted completely into a chloride, whose quantity is to be determined as a chloride of silver. The borates of the alkaline earths are, like most of the other borates, with difficulty soluble in water,—not a single one is insoluble, on which account boracic acid cannot be completely precipitated by any metallic salt.

The soluble borates give, with *the protosalts of calcium, barium, lead, and silver, the subsalts of mercury and the sesquisalts of iron,* when in moderately dilute solution, white or yellowish precipitates, which are all readily soluble in acids and in ammoniacal salts. The alkaline borates dissolve, by fusing, many metallic oxides, forming double salts (glasses, or beads) of characteristic colors.

If a borate which has been moistened, is heated along with a mixture of one part of fluorspar and four and a half parts of bisulphate of potassa on a platinum wire, the fluoride of boron thus formed gives to the flame of the blowpipe an evanescent, slight green color.

For the detection of boracic acid in soluble or insoluble compounds, the pulverized substance is warmed along with some concentrated or only slightly diluted sulphuric acid, alcohol is added and inflamed; even if there be only a small quantity of boracic acid present, the flame will show a green color, especially on its being stirred. Or, strips of tumeric paper may be dipped in the solution of the substance in chlorhydric acid,—these become brown when dry, if boracic acid is present.

Boracic acid is entirely volatilized from its salts, as a fluoride of boron or boracic ether, by warming with fluohydric and sulphuric acid, or less perfectly with sulphuric acid and alcohol. By fusion with an alkaline carbonate, the natural insoluble borates are completely decomposed. Boracic acid is separated from phosphoric acid by precipitation of the latter as the phosphate of ammonio-magnesia, the boracic acid remaining in solution.

10. Silicic Acid, SiO_3, and the Silicates.

Silicic acid is found very abundantly in nature, sometimes free, sometimes united in various proportions, with the most dissimilar bases (in the Silicates), also in a soluble form in well and mineral waters, and in the ashes of vegetable and animal substances. It is divided into *crystalline* silicic acid (Rock-crystal, Quartz), and that which is *amorphous* (Opal, Hyalite, etc.); both modifications are found in Chalcedony, Agate, and Flint. When artificially prepared it is always amorphous, — a white powder, resisting fire, perfectly insoluble in water as well as in all the acids, excepting fluohydric acid; — it is much easier dissolved in caustic or carbonated alkalies than the crystalline modification.

Silicic acid forms with water a hydrate — the so-called soluble silica; this hydrate is soluble in water as well as in all acids; it is always formed when an alkaline silicate in an aqueous solution is decomposed by an acid, or when the fluoride, chloride, or sulphide of silicium is decomposed by water, and it mostly separates, as a jelly or in gelatinous flakes, losing the water combined with it even on being dried in the air, or still quicker indeed at a higher temperature, and at the same time loses also its property of being dissolved by water (or hydrated acids).

The silicates, with exception of the silicate of potassa and of soda, are perfectly insoluble in water. The aqueous solution of an alkaline silicate has an alkaline reaction, and gives, with the salts of *lime*, *baryta*, *lead*, and *silver*, white precipitates, which are soluble in dilute chlorhydric or nitric acid, and are decomposable by concentrated acids with the separation of the silicic acid.

Chloride of ammonium and *carbonate of ammonia*, also (though less perfectly) *sulphide of ammonium* and *sulphide of potassium*, precipitate silicic acid, in a gelatinous or flaky form, from the solutions of the alkaline silicates; *lime-* or *baryta-water*, or a solution of *alumina* in *potassa*, or of *the oxide of Zinc* in *ammonia*, precipitate insoluble double silicates.

If a *dilute* aqueous solution of an alkaline silicate is saturated with chlorhydric or nitric acid, all the silicic acid remains in the solution as the hydrate; if this solution is evaporated down to a certain point, or a somewhat concentrated solution is mixed with the acid, then the silicic acid separating, usually forms a jelly — sometimes a flaky powder, which on *perfect* evaporation (in a water bath) becomes *insoluble* silica. If this dried mass (it must not be ignited) is treated with water, the chlorides of the metals, or the nitrates of the alkalies or alkaline earths are completely dissolved, whilst pure silica remains; in the presence of such bases, as, like alumina, the sesquioxide of iron, magnesia, etc., form on evaporation (with the loss of their acids) basic compounds that are insoluble in water, it is very essential for the complete separation of the silicic acid that the dried mass should be first moistened with some concentrated acid, — after standing a half hour all the bases present which had been united with silicic acid can be dissolved in water by the aid of heat. (Separation of silicic acid from all basic oxides, which are soluble in chlorhydric or nitric acid.)

The gelatinous, as well as the slightly-dried, amorphous silicic acid, is very readily and copiously dissolved in caustic or carbonated alkalies, especially on boiling; the strongly ignited or the finely pulverized crystalline silicic acid is with somewhat more difficulty soluble in alkalies, — but it passes completely over into the soluble modification, when it is fused (either by itself or in combination with bases) along with an excess of an alkaline carbonate.*

Analysis of Silicates. — Some of the silicates, which appear in nature or are produced by art, are crystallized, others form crystalline or amorphous (vitreous) masses of manifold colors, which contain as a rule many different bases, and comport themselves with reagents according to the quantity or nature of these bases.

One class of these silicates is decomposable, when in a finely pulverized condition, by acids, in such manner that all their silicic acid is separated in a soluble form, as a jelly or in flakes. To this class belong the *Zeolites*, which are remarkable for containing water, also most of the *slags*, and especially all those silicates in which a strong base is present in a quantity greatly exceeding that of the silicic acid. Many silicates, as Vesuvian or Garnet, are decomposable by acids only after ignition or fusion; the Zeolites, on the other hand, are very difficult to dissolve in acids, if their water has been removed by ignition. There are, however, some exceptions, as Prehnite is more easily decomposed by acids, after ignition, than when not ignited and containing water.

In the analysis of Zeolites, slags, and other silicates decomposable by acids, the compound (being finely pul-

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* This solubility of silicic acid in caustic or carbonated alkalies, requires that care should be taken, in delicate analyses, that fluids which contain caustic or carbonated alkalies should not be boiled or evaporated in glass or porcelain vessels, but only in platinum basins.

verized) is digested with an excess of concentrated chlorhydric acid, until the granular or arenaceous character of the mineral has disappeared (recognized by rubbing with a glass rod) and only the gelatinous or flaky silicic acid is left behind. There is always dissolved by this process a portion of the silicic acid in the chlorhydric acid; in order to make this insoluble, the liquid is evaporated to dryness in a water bath (being stirred towards the last), the perfectly dried mass is uniformly moistened with some concentrated chlorhydric acid, warmed after standing a half hour with water, and the pure separated silicic acid is filtered off.

Moderately dilute sulphuric acid decomposes most of the silicates more easily than chlorhydric acid; but if a quantity of lime is contained in the mineral, the analysis is involved in greater difficulties, on which account the application of chlorhydric acid is preferable. Nitric acid is used when the silicates contain the oxide of lead.

The other class of silicates is either decomposed with difficulty, partially or not at all, by digestion with acids; such silicates must, for the detection and determination of their bases, *be made decomposable* by chlorhydric acid. This is accomplished in most cases by fusing the finely powdered or washed compounds in a platinum crucible, along with three or four times its weight of dry carbonate of soda, or a mixture of two parts of carbonate of potassa and one and a half parts of carbonate of soda. After fusing from a quarter to a half hour, the mass, when cold, is placed in a beaker glass, and excess of chlorhydric acid is gradually added to it, and since, in consequence of the evolution of carbonic acid gas, there might be some loss of material, it is prevented by a watch-glass or a porcelain dish. By gentle digestion, the decomposition of the fused mass is promoted; the complete decomposibility of the mineral is recognized when only the flaky silicic acid remains undissolved, which feels soft if a glass rod is applied to it, whilst on the other hand the undecomposed powdered mineral scratches against the glass on stirring with a glass rod, of which the ear gives sure information. The liquid, as in the analysis of Zeolites, with the silicic acid swimming in it, is evaporated to perfect dryness (being constantly stirred) at first in a water bath, and at last in a sand bath, the dried mass is moistened again with concentrated chlorhydric acid, after standing a half hour it is warmed with water and the silicic acid filtered off; — it must be perfectly dry before ignition.

Some natural silicates — as Zircon, Cyanite, Cymophane — require for their complete decomposition a continuous, active fusion with an alkaline carbonate; the decomposition is facilitated by an addition of hydrate of potassa or of soda, which is placed in the middle of the mixture firmly pressed in the platinum crucible. In silicates, which contain alkalies — if the silicic acid is to be determined at the same time with the bases — the decomposition is accomplished by four or five times the weight of hydrate or carbonate of baryta, or, less effectively, by nitrate of baryta. The silicic acid is separated from the decomposed mass, exactly as described above, and then the baryta is thrown down from the chlorhydric acid solution by the careful addition of sulphuric acid. The bases are determined in the filtrate.

Or the silicic acid and all the bases (excepting the alkalies) are detected on decomposition with an alkaline carbonate, a second portion being decomposed by fluohydric acid for the determination of the alkalies. For this operation, the finely powdered silicate to be tested is exposed, in a platinum dish, (being drenched with dilute sulphuric acid,) to the fumes of fluohydric acid which are disengaged from fluorspar by means of concentrated sulphuric acid in a lead apparatus. After one or two days action there is obtained a solution, as clear as water, of the sulphates of those bases which were held by the silicates. This solution, with the addition of some sulphuric acid, is evaporated to dryness, and the bases separated by such methods as their properties indicate.

Many mixed silicates, as clink-stone, argillaceous schist (clay slate), etc., contain a silicate which is decomposable by acids — as a Zeolite — along with another which is not so decomposed. These are first decomposed by digesting with concentrated chlorhydric acid, and the solution, which contains all the bases of the decomposable portion, is diluted with water and filtered. The residuum, composed of the undecomposed mineral and the silicic acid that has been separated, is added by portions to a boiling solution of carbonate of potassa (more of the alkali being added also from time to time) and filtered while hot. The alkaline solution yields, after being evaporated with chlorhydric acid, the silicic acid of the decomposable silicate; the insoluble portion is treated, in a further analysis, as a silicate undecomposable by acids.

In many silicates, attention must be paid to the other constituents, besides the water and the silicates of metallic oxides; thus Tourmaline contains fluorine and boracic acid, Nosean chlorine and sulphuric acid, Cancrinite carbonic acid, Hauyne and Ultramarine chlorine and sulphur; very many fossils contain phosphoric acid. Tourmalines are, after ignition, whereby the fluoride of silicium is evolved, decomposed by fluohydric acid.

Silicic acid is separated from *titanic acid* by fusion along with bisulphate of potassa in a platinum crucible, whereupon the titanic acid can be extracted by water, while the silicic acid remains undissolved.

Recognition of silicic acid. Silicic acid is known by its complete insolubility in acids, and by its comportment with phosphate of ammonia-soda on platinum wire before the blowpipe. Silicic acid is very slightly soluble in fusing phosphate of ammonia-soda; the largest portion of it swims in the pearl as a spongy mass (silica-skeleton), which is more readily perceptible when the glass is red-hot than when it is cold. The base is removed from the silicates by the phosphoric acid, with a deposite of the silica-skeleton. Pure silicic acid always produces a clear, never an opaque bead. Silicic acid is slowly but perfectly soluble in borax. Silicic acid, or silicates *poor* in bases, with (not too much) soda, is fused, with foaming, into a clear bead, which remains clear when cold. Pure silicic acid leaves no residuum when evaporated with excess of fluohydric acid; it is perfectly soluble in boiling, aqueous solutions of caustic or carbonated alkalies (a platinum basin being employed) — the saturated solution gelatinizes on cooling; if an earth or a metallic oxide is present, the silicate remains undissolved.

11. SILICOFLUOHYDRIC ACID, $3\,HF,\ 2\,SiF_3$, AND THE SILICOFLUORIDES.

The acid is produced by the action of fluohydric acid on silicic acid or the silicates, or by the decomposition of the terfluoride of silicium by water ($3\,SiF_3 + 3\,HO = 3\,HF,\ 2\,SiF_3 + SiO_3$). Silicofluohydric acid is a liquid, with an acid reaction completely volatilizable in a platinum vessel as the terfluoride of silicium and fluohydric acid; on evaporation of the acid (or of the silicofluorides mixed with chlorhydric acid) in glass vessels, these are corroded by it.

The silicic fluorides are mostly soluble in water, and are decomposable by alkalies and acids; *the salts of potassa, soda, lithia,* and *baryta* are precipitated gelatinous by silicofluohydric acid, and, on the addition of alcohol, perfectly as silicofluorides, ex. gr. $3\,BaF, 2\,SiF_3$. (The most precise method of separating baryta from strontia, depends on the precipitation of the baryta by means of silicofluohydric acid).

The silicofluorides are decomposed at a red heat with the disengagement of terfluoride of silicium, while the metallic fluoride remains. The Borofluorides comport themselves in a similar manner.

12. Oxides of Carbon.

Carbon is found as the Diamond, Graphite, and Anthracite; it is a constituent of *all* organic compounds; exists as carbonic acid in the atmosphere, in all well and mineral waters, also in combination with lime, baryta, magnesia, the protoxide of iron and manganese, etc.

The principal characteristics of *carbon* are its insolubility in acids and alkalies, its property of resisting fire in closed vessels, and its conversion by combustion in contact with oxygen, or on fusion with nitre, into carbonic acid, in the latter experiment detonation takes place. Every compound containing carbon yields, on being ignited with protoxide of copper or the chromate of lead, carbonic acid which is tested by lime-water or acetate of lead, and which is easily absorbed by caustic potassa. Amorphous carbon is always black.

a. CARBONIC ACID, CO_2. — This is a colorless, coercible gas, of a weak, suffocating odor, — it is heavier than atmospheric air. It is somewhat soluble in water, — the solution turns litmus paper temporarily red, and gives up all its carbonic acid on being boiled, and most of it by mere exposure to the air. An aqueous solution of free carbonic acid gives, with lime water, a white precipitate, again soluble in excess of the carbonic acid water. (Its recognition in mineral waters.) Acetate of lead produces, even in very dilute solutions, a white turbidness. Carbonic acid is perfectly absorbed by potassa-lye and solid hydrate of lime.

The alkaline carbonates are the only neutral carbonates which are soluble in water (giving it an alkaline reaction); a neutral carbonate of an alkali produces precipitates with all the metallic salts. Some carbonates (namely, those of the alkaline earths, of magnesia, and of the protoxide of iron and of manganese) are soluble in free carbonic acid, making bicarbonates; the solution becomes turbid on boiling, with a precipitation of the neutral or basic salt.

The solution of *a neutral carbonate* is precipitated white, even though very dilute, by *the salts of lime, baryta, magnesia*, and by those of *the protoxide of lead* and of *silver*, — brick-red by *the protochloride of mercury*; all these precipitates are readily soluble in nitric or acetic acid. The carbonates of the alkaline earths, as well as the carbonate of magnesia, are also soluble in chloride of ammonium; carbonate of lime is reprecipitated from such solution by free ammonia.

A solution of a *bicarbonate* affords no precipitate with *sulphate of magnesia*, and a white one, forming gradually, with *the protochloride of mercury*; *the salts of lime* are not precipitated by an alkaline bicarbonate, except when the solution is very dilute. Alumina and sesquioxide of iron are precipitated by the bicarbonate of soda.

The solid carbonates (also their solutions if not too dilute) are easily recognized by the fact that they are decomposed by all acids *with effervescence.* The gas evolved is almost *inodorous,* and produces white turbidness in *lime water* or *acetate of lead.* The *Cyanates* evolve carbonic acid, along with acids, but it is always accompanied with cyanic acid of a penetrating odor and the residuum contains an *ammoniacal salt.*

Some natural carbonates (*Spathic Iron, Dolomite*), are only decomposed with effervescence on being warmed along with concentrated acids. The neutral alkaline carbonates, as well as the carbonate of baryta, remain undecomposed when ignited by themselves; the carbonate of lime loses its carbonic acid when strongly ignited over the spirit-lamp, — in the presence of charcoal the decomposition is much more easily accomplished, with the formation of carbonic oxide; all the other carbonates are very easily decomposed by ignition.

Carbonic acid is determined by the loss of weight which its compounds suffer, when they are decomposed, by means of a moderately dilute acid, in an apparatus which allows of exact weight of the dried residuum after the escape of the carbonic acid. The carbonic acid dissolved in mineral waters is removed by precipitation, with a mixture of chloride of calcium and ammonia. In a mixture of sulphurous (or sulphydric) acid gas and carbonic acid gas, the former is completely removed by the binoxide of manganese or of lead, or by the protoxide of mercury (being spread out when moist on a porcelain rod and dried), as also by a concentrated solution of bichromate of potassa mixed with sulphuric acid (the sulphydric acid may be also removed by protosulphate of copper). Carbonic acid gas is separated from gases that are not acid by hydrate of potassa, which absorbs it completely.

b. CARBONIC OXIDE, Co.—Formed by imperfect oxidation of carbon or the deoxidation of carbonic acid. It is a colorless gas (burning with a bluish flame), which is absorbed by melting potassium, as well as by a solution of subchloride of copper, Cu_2Cl, in ammonia or by the subsulphite of copper. Exploded along with one half volume of oxygen, one volume of carbonic oxide forms one of carbonic acid.

13. OXYGEN. O.

A constituent of the atmosphere, of water, and also of most chemical compounds. It is a colorless, inodorous, and permanent gas, readily recognized by the fact that a flickering spark is kindled in it, and that it produces yellowish red vapors when mixed with nitric oxide. Mixed with double its volume of hydrogen and ignited, it explodes, forming water, all the gas disappearing.

Oxygen is only slightly soluble in water; it is readily absorbed by *phosphorus*, by metallic copper when in a state of ignition or when moistened with dilute sulphuric acid, by a solution of *subchloride of copper* in *ammonia* or of gallic acid in *caustic potassa*, by *the hydrated protoxide of iron* suspended in an alkaline fluid, by *alkaline sulphides*, less quickly by shaking with finely divided and moistened *metallic lead*. (Eudiometry).

14. Hydrogen. H.

A colorless, inodorous, very light, permanent gas, burning with a faint blue flame, (forming water). It is only very slightly soluble in water. It forms water when mixed with half its volume of oxygen (in contact with platinum sponge which has been made in the form of balls with clay, slowly, and with detonation on ignition); with an equal volume of chlorine it explodes in the sunlight, forming chlorhydric acid gas, — the mixture of the two gases is slowly absorbed by water in the dark. On passing hydrogen gas (or a mixture of gases containing hydrogen) over ignited protoxide of copper, also on the ignition of organic combinations, containing hydrogen, mixed with excess of protoxide of copper, *all* the hydrogen is converted into *water*, which can be perfectly taken up by dry chloride of calcium. (Determination of the combination of water, and of hydrogen in organic compounds). The compounds of hydrogen with carbon afford at the same time carbonic acid.

Of the gaseous *hydrides of carbon*, that called *Olefiant gas* C_4H_4, burning with a very luminous flame, is perfectly absorbed by fuming sulphuric acid; along with an equal volume of chlorine it is condensed (even in the dark), forming oily drops, $C_4H_4Cl_2$. That which burns with a pale blue flame, the *marsh* (or *ditch*) *gas* C_2H_4 is not absorbed by fuming sulphuric acid, and is not condensed, along with chlorine, over water in the dark, though this occurs in the light with the formation of carbonic acid. Mixed with two volumes of oxygen and exploded, one volume of marsh gas produces water and one volume of carbonic acid gas.

15. Water. HO.

Pure water is colorless and tasteless, with no reaction on vegetable colors. It can be evaporated on platinum foil without any residuum.

For the *detection* of water in fixed, non-volatile substances, in minerals and salts, these are heated, to low ignition, in a dry glass tube closed at one end and held obliquely over the spirit-lamp, when the smallest quantity of water can be recognized, in the cooler portion of the tube, in the form of mist or even drops. Organic compounds must not be heated too strongly as they suffer a complete decomposition.

The *determination* of water is carried on in such compounds as are non-volatile and undergo no further change at a high temperature, simply by means of the loss of weight which takes place in drying them at a low or high temperature, or even on ignition, according to the nature of the compound. In such compounds as are decomposed by this procedure, the water is received in a weighed chloride of calcium tube, if the products of the decomposition (ex. gr. ammonia) are not likewise absorbed by chloride of calcium. In organic compounds, the determination of the water is chiefly accomplished, along with that of the hydrogen, by one operation.

16. Organic Acids.

The compounds which the organic acids form with alkalies and alkaline earths are converted, on ignition, into carbonates, and become black whilst carbon is separated. The oxalates are decomposed when pure without any discoloration. The characteristic reactions of the more important organic acids are as follows:—

a. Oxalic Acid, HO, C_2O_3.—The oxalates which are soluble in water or in acetic acid, as also free oxalic acid, give a white precipitate with *lime-water* or the soluble *salts of lime* (even the sulphate), ($CaO, C_2O_3, 2$ aq.), which is insoluble in ammonia, ammoniacal salts, and in acetic acid, somewhat soluble in free oxalic acid, and very soluble in chlorhydric or nitric acid; in a solution of a protosalt of copper (the protochloride) it is gradually converted into the oxalate of copper (without its being dissolved); this transposition follows also on boiling it with other metallic salts.

Nitrate of silver produces a white precipitate, soluble in nitric acid and in ammonia.

If oxalic acid or an oxalate is warmed along with excess of concentrated sulphuric acid, it disengages, without any discoloration, carbonic acid and carbonic oxide. $(C_2O_3 = CO_2 + CO)$.

b. Tartaric Acid, $2HO, C_8H_4O_{10}$.—Tartaric acid is decomposed by heat, with the evolution of a peculiar, characteristic odor.

Tartaric acid (and the tartrates) is precipitated, by an excess of *lime-water*, white ($2CaO, \overline{T}$). The same precipitate is produced on mixing a *neutral tartrate* with *chloride of calcium*, but is not produced with the sulphate of lime. Tartrate of lime is soluble in acids, even in free tartaric acid, and in ammoniacal salts; it is completely soluble in cold *potassa-lye*,—this solution becomes gelatinous on being boiled, but when cold, is again clear. Tartrate of lime is insoluble in chloride of copper.

If a neutral tartrate be mixed with a salt of potassa and a free acid (the acetate of potassa and acetic acid answer best), a crystalline precipitate is produced (if the solution is not too dilute) of the bitartrate of potassa (vide page 2), which is very soluble in mineral acids and in alkalies.

Tartaric acid, like many other non-volatile organic acids, prevents the precipitation by alkalies, of the sesquioxide of iron, the protoxide of copper, and many other metallic oxides.

Racemic acid is distinguished from tartaric acid only by the insolubility of its lime salt in the salts of ammonia or in free racemic acid.

c. CITRIC ACID, $3\,HO, C_{12}H_5O_{11}$.—An aqueous solution of citric acid when cold is *not* precipitated by lime-water (nor is its dilute solution when neutralized by ammonia precipitated by the salts of lime); on heating the liquid to ebullition, there is produced (so far as it is neutral, or contains excess of lime-water or even of free ammonia) a white precipitate of the basic citrate of lime, insoluble in potassa, with difficulty soluble in ammoniacal salts, soluble in free acids and in the protochloride of copper.

d. MALIC ACID, $2\,HO, C_8H_4O_8$.—When malic acid is heated, it is decomposed with the formation of a crystalline sublimate of parafumaric acid, while fumaric acid remains behind.

An aqueous solution of malic acid, or of the malates, is neither precipitated by *lime-water*, nor by *chloride of calcium*, when cold or when heated; on the addition, however, of alcohol to a solution of a malate mixed with chloride of calcium, there is produced a white precipitate of the malate of lime, which is soluble in the protochloride of copper. Also when a solution of malic acid (ex. gr. in the juice of the sorb or service berries) nearly neutralized with milk of lime, is boiled for a long time, a neutral malate of lime is precipitated.

The malates give a white precipitate, gradually becoming crystalline, with the acetate of lead, which, if it be mixed with no other insoluble compound, melts, on heating the liquid to ebullition, forming a transparent mass.

e. Kinic Acid, $C_{14}H_8O_8$.— Only found in genuine cinchona bark. For its detection, the powdered bark is boiled along with milk of lime, the extract is evaporated, and the syrupy residuum is distilled in a moderate-sized retort along with sulphuric acid (somewhat diluted) and binoxide of manganese. If kinic acid is present, the first portion of the distillate is yellow or forms yellow crystals of Kinon $C_{12}H_4O_4$, whose solution is made a blackish-brown by ammonia, or a clear green by chlorine water.

f. Meconic Acid, $3\,HO, C_{14}HO_{11}$.—Is found in Opium.—Solutions of Meconic acid or of its salts are colored blood-red by the sesquisalts of iron; the color differs from that produced by sulphcyanic acid, since it disappears in chlorhydric acid and is not made yellow by the terchloride of gold.

g. Tannic Acid.—This acid is precipitated in a pasty form from its aqueous solutions by the mineral acids,—the precipitate being insoluble in excess of the latter.

With *solution of gelatine* it gives a white elastic precipitate, which is gray in excess of the tannic acid. It is entirely removed from its solutions by *animal membrane*. (Distinction from gallic acid, and determination of tannic acid by the increase of weight of animal membrane in solutions of the acids.)

The sesquisalts of iron give a bluish-black precipitate with tannic acid; a precipitate is produced by the protosalts of iron if exposed to oxidizing influences.

Tartar emetic gives a white, gelatinous precipitate.

Tannic acid forms, with the bases of most organic salts, white compounds, which are insoluble in water, though soluble in acetic acid.

Tannic acid is soluble in water, alcohol, and anhydrous ether; its syrupy solution in the latter does not mix with additional ether.

h. Gallic Acid, $C_{14}H_6O_{10}$. — Solutions of this acid are colored a deep, dark blue by the sesquisalts of iron and precipitated a blackish-blue by the protosalts. It is *not* precipitated by gelatine or animal membrane. An alkaline solution of gallic acid gradually becomes on exposure to the air (on account of the absorption of oxygen) yellow, green, red, and at last brownish-black.

i. Succinic Acid, $2\,HO$, $C_8H_4O_6$. — This acid is sublimed by heat, and is soluble in water, alcohol, and ether.

The sesquichloride of iron produces a brownish, voluminous precipitate, in perfectly neutral solutions, which is completely soluble in acids; ammonia extracts the succinic acid from it, and the sesquioxide of iron or the basic salt remains undissolved.

A mixture of alcohol, ammonia and chloride of barium produces a white precipitate in solutions of succinic acid or of its salts.

k. Benzoic Acid, HO, $C_{14}H_5O_3$. — This acid can also be sublimed, and is with difficulty soluble in cold water, on which account it is precipitated by acids, as a white crystalline powder, from moderately dilute solutions of its salts.

It comports itself with *the sesquichloride of iron* like succinic acid. Both acids, on being heated, evolve strong vapors, which excite coughing.

l. Acetic Acid, HO, $C_4H_3O_3$. — The salts of this very volatile acid are all soluble in water, — the salts of the protoxide of silver and the suboxide of mercury are the only salts with difficulty soluble. Most of the acetates when heated evolve aceton which is inflammable, and has a characteristic odor ($2\,C_4H_3O_3 = C_6H_6O_2 + 2\,CO_2$).

Sesquisalts of iron give a dark-red color, with solutions of the acetates (not with free acetic acid), which color disappears on the addition of chlorhydric acid. When heated by itself, or when an excess of ammonia is present, all the sesquioxide of iron is thrown down from the red solution.

If an acetate or its concentrated aqueous solution be warmed along with excess of sulphuric acid and alcohol, *acetic ether* is produced ($C_4H_3O_3, C_4H_5O$), which is readily recognized by its odor.

For the reaction which depends on the formation of the oxide of kakodyl, which however is also produced with other acids (ex. gr. butyric) resembling acetic acid, see page 82.

An aqueous solution of free acetic acid, when digested with excess of protoxide of lead, yields a liquid with an alkaline reaction, — a peculiarity which is not possessed by formic and lactic acid.

For the certain detection of acetic acid in mixed compounds, they are subjected to distillation along with water with which some dilute sulphuric acid is mixed, if free acid is not already present. Very dilute solutions, if they are acid, are first neutralized by carbonate of soda and then concentrated by evaporation.

If acetic acid is to be detected in a mixture of other volatile acids (of the formula $C_nH_nO_4$, as butyric acid, valerianic acid, etc.), the aqueous solution of the free acids is *partially* neutralized by potassa (taking according to the supposed quantity of one acid or the other the $\frac{1}{10}$, $\frac{1}{5}$, $\frac{1}{3}$, or $\frac{1}{2}$), and the neutralized portion, together with the rest of the mixture of the acids, is submitted to distillation, when the acetic acid (as a binacetate) is always left entirely or in part in the residuum, whilst butyric and valerianic acid are distilled over either partially or completely. A mixture of butyric and valerianic acid being treated in this way, the more volatile, butyric acid distils over, whilst the valerianic acid remains back entire or in part.

FORMIC ACID, HO, C_2HO_3.—This acid comports itself in many respects very like acetic acid. With the *sesquichloride of iron*, the formates produce the same red color as the acetates. With the protoxide of lead it forms only a neutral salt (with no alkaline reaction).

Formic acid can be recognized in a free condition, and also in its salts, by its property of reducing the oxides of the precious metals, with the disengagement of carbonic acid.

A fluid containing formic acid, if warmed with *nitrate of silver* or *subnitrate of mercury*, after effervescence, shows the deposition of the pure metal either black (silver) or gray (mercury).

By being warmed with *protochloride of mercury*, the subchloride is precipitated, which is reduced to the metallic condition on boiling. In this way, by an excess of finely powdered protoxide of mercury, formic acid can be completely removed from a mixture of acids; acetic acid and the other volatile acids of the formula $C_n H_n O_4$ are not decomposed in this way.

For the detection of small quantities of formic acid in liquids, which contain also other organic compounds, they are subject to distillation, being previously acidulated with some *dilute* sulphuric acid, if they are not already acid. The distillate is saturated with carbonate of soda, then concentrated by evaporation and tested.

Formic acid, or its salts, warmed with concentrated sulphuric acid, is resolved into water and carbonic oxide ($C_2HO_3 = 2CO + HO$).

n. Lactic Acid, $HO, C_6H_5O_5$. — This acid is very soluble in water, alcohol, and ether. It is non-volatile, — its salts are completely soluble in water, and the lactates of zinc and lime are easily crystallized, and answer excellently for the recognition of lactic acid.

For the detection of lactic acid in animal substances (in the fluids of the flesh, in the blood, urine, etc.), these are evaporated in a water bath, and the residuum treated with a solution of oxalic acid in alcohol; the filtered liquid is digested with protoxide of lead, and the filtrate (which contains the lactic acid as a salt of lead), after the removal of the protoxide of lead by sulphydric acid, is evaporated and boiled along with the protoxide of zinc, or mixed with excess of milk of lime, and the clear solution left to crystallize.

Or the residuum, obtained by evaporation in the water bath, is treated carefully with alcohol, the alcoholic solution evaporated to a syrup, mixed with an equal volume of dilute sulphuric acid (composed of equal volumes of water and acid), and then three or four times the volume of alcohol is added. The alcoholic solution containing lactic acid is now mixed with ether, which is added until no more turbidness is produced by its addition, filtered, the alcohol and ether distilled off, and the residuum evaporated to a syrup in a water bath. This syrup is mixed with one half its volume of alcohol, and then with five volumes of ether, which dissolves the lactic acid almost pure. After the evaporation of the ether, it is saturated with milk of lime and the filtrate is exposed to crystallization at a gentle heat. The gypsum, which is mixed with the lactate of lime, is removed by dissolving the latter in alcohol. The most certain mode of recognizing lactic acid, is the elementary analysis of the pure salt.

Warmed along with excess of concentrated sulphuric acid, lactic acid evolves pure carbonic oxide gas, and with excess of nitric acid it is converted into oxalic acid.

o. Uric Acid, $2HO$, $C_{10}H_2N_4O_4$. — This is a white, crystalline powder, which is with great difficulty soluble in water and dilute chlorhydric or acetic acid; insoluble in alcohol and ether; it is soluble with comparative ease in alkalies as well as in alkaline salts, — from which solution, acids precipitate it. Uric acid is soluble in moderately concentrated nitric acid with the disengagement of gas; if the solution is evaporated to dryness and the residuum moistened with a *little* ammonia, a beautiful *purplish-red* color arises (from the formation of Murexide) which is made a purplish-blue by caustic potassa. By means of this reaction even very small quantities of uric acid can be recognized.

For the detection of uric acid in urine, the latter (about one half pound) is mixed with some chlorhydric acid, when the uric acid separates in a day or two. It is extracted from urinary sediments or concretions by warming them along with some dilute potassa lye, and then saturating the filtrate with chlorhydric acid. Albuminous fluids (serum of the blood) are evaporated in a water bath, and the residuum, after it has been exhausted by alcohol, is boiled with water; the aqueous extract, concentrated by evaporation, suffers the uric acid to be precipitated on the addition of some acetic acid, when the uric acid can be easily tested by nitric acid and ammonia.

On fusion with hydrate of potassa, uric acid evolves ammonia; the residuum contains, if it has not been too strongly heated, cyanide of potassium and cyanate of potassa.

PART THIRD.

COURSE OF QUALITATIVE CHEMICAL ANALYSIS.

I. Preliminary Examination of Solids, and Reduction of the same to the Fluid condition.

The analyst, in a qualitative examination of a solid, has first of all to obtain information as to its general nature by a close observance of its physical properties. This information is secured by *an examination in the dry way* (always necessarily preceding the proper qualitative analysis in the wet way), which includes, along with the simultaneous observance of the physical nature (form, color, lustre, hardness, specific gravity, etc.), *the comportment of the substance at a high temperature*, either alone, in the presence of the air, or with other chemical compounds, which effect its decomposition or merely its simple solution.

This examination is conducted according to the tables (tables I. and II.), appended to this treatise, by which the general chemical nature of the body to be examined is established, and the qualities of the metals or metallic oxides, or even some of the metalloids present are specially pointed out; the ninth table serves exclusively for *the examination for acids*, and especially for the *volatile acids*, or such as yield volatile products of decomposition, on being heated along with concentrated sulphuric acid. The management of these tabular views requires no explanatory commentary; they explain themselves, and continued practical employment of them gives the necessary certainty to the results which are obtained by their use. After it has been ascertained by the examination in the dry way to what class of compounds the body to be examined belongs, it is next to be determined how to bring it into the form alone suited for the qualitative analysis in the wet way, — namely, the fluid condition. In this operation the *preparation* of the substance, in many cases, bringing it in a condition which is most suitable for solution, must first take place; it must, if its nature permit, be *finely pulverized*, and sometimes *even levigated*. This is indispensable with minerals, especially the silicates, as also all other compounds which are either with difficulty soluble, insoluble, or with difficulty decomposable.

It is now first to be tried, whether the substance is *completely*, *partially*, or *not at all* soluble in water. In case of partial solubility, the fluid filtered off from the undissolved portion and evaporated on polished platinum foil, leaves a residuum, which is clearly perceptible, — where there is perfect insolubility this does not take place. Moreover the aqueous solution is to be tested, whether it has a *neutral*, *acid*, or *alkaline* reaction with litmus paper. If a substance is only partially soluble in water, the constituents of the dissolved and of the undissolved portions are to be ascertained separately.

If it does not dissolve in water, the effect of *dilute* or *concentrated chlorhydric acid* is tried, attention being paid to the kinds of gases developed in the process. The *compounds of carbonic acid* disengage carbonic acid gas with effervescence, the binoxides or *the chromates* chlorine, *the cyanides* cyanhydric acid, many *sulphides* sulphydric acid gas, *the sulphites* and *the hyposulphites* sulphurous acid gas, — the latter with the simultaneous deposition of sulphur; some of the *reguline metals* (zinc, iron, tin, etc.), with chlorhydric acid evolve hydrogen; those containing arsenic, arseniетted hydrogen, — those containing antimony, antimonietted hydrogen. Chlorhydric acid either completely dissolves the substance or leaves a residuum; in the latter case usually a complete separation of one or more constituents has been effected, and for this reason the insoluble residuum must be separated from the liquid and be examined by itself; an effort must be made to render it soluble by further treatment (table III.).

If the substance is insoluble in chlorhydric acid (or leaves a residuum insoluble in it), its comportment with nitric acid or aqua regia must be tried. Many sulphides, on treatment with nitric acid, yield their *sulphur*, which, by sufficient continued action, collects as yellow drops and swims in the liquid, or wholly disappears; then sulphuric acid newly formed is always found if the metallic oxide produced in the process forms with it no compound insoluble in the acid. Thus *sulphide of lead* (lead glance) yields the sulphate of lead on treatment with nitric acid, *sulphide of tin*, or *tersulphide of antimony*, are converted into *white oxides; sulphide of mercury* is not acted upon by nitric acid, but is very easily dissolved by aqua regia.

The reguline metals are almost all soluble in nitric acid; if such a metal is not acted on by nitric acid, then it must contain *gold, platinum, iridium*, or the rare metals contained in platinum ores. *Gold* and *platinum* are dissolved by aqua regia, *palladium* also by nitric acid. *Tin* and *antimony* are converted into white oxides (insoluble in excess of the acid), on treatment with nitric acid, — they are easily dissolved by aqua regia (or chlorhydric acid and chlorate of potassa) if an excess of nitric acid is avoided; silver is converted, by aqua regia, into the chloride.

If the substance is neither soluble nor decomposable in any of the acids mentioned, even on long digestion at a moderate heat, it is either *a sulphate* (baryta, strontia, lime, or protoxide of lead), *a chloride, bromide,* or *iodide* (silver), *a fluoride* (Fluorspar), or *silicic, tungstic, titanic, tantalic, niobic,* or *pelopic acid, alumina, sesquioxide of chromium, binoxide of tin, antimonic acid* (or their compounds), *irid-osmium* (the residuum from platinum ores), or *carbon* itself. Many oxides (sesquioxides of aluminium, chromium, and iron) become, on violent ignition in acids, just as insoluble as their crystalline forms which appear in nature. Their reduction to the soluble condition is effected according to table III.

II. QUALITATIVE EXAMINATION OF THE SUBSTANCES PRESENT IN SOLUTION.

After having succeeded, by one or other of the methods pointed out, in effecting a solution of a substance, the question to be answered is, What are the components of the solution? In minerals, attention is at once directed to their known components, since sufficient indications are afforded by their mineralogical determination, and in most solid chemical compounds, by their comportment, during the preliminary examination in the dry way, and towards solvents. But this is not the case with all. The question as to the presence of this or that body is answered by bringing the solution in contact with known compounds, which are called *reagents.* By the changes and phenomena produced in this way, which depend on the formation of new compounds of known properties, the presence of a body is determined. It is manifest, that the solution of the substance to be examined should not be brought at random into contact with any reagent we please, but that a certain order or succession of reactions must be observed. Comportment with the *general reagents*, constitutes the basis of this order, by whose application it is aimed to separate the constituents present in the solution into certain groups, whence their further separation and recognition is facilitated and prepared.

The general reagents are: —

a. *For the metallic oxides:* sulphydric acid, sulphide of ammonium (or sulphide of potassium), carbonate of ammonia, caustic potassa, and ammonia.

b. *For the acids:* concentrated sulphuric, chlorhydric, or nitric acid, chloride of barium (or nitrate of baryta), chloride of calcium (or lime-water), sulphate of magnesia (or chloride of magnesium), sesquichloride of iron, and nitrate of silver. The solution of indigo serves for the recognition of acids rich in oxygen, or freely evolving chlorine.

In the qualitative analysis of *fluids* (that is, solutions which we have not prepared), it is necessary to try: —

1. Whether they contain *volatile* or *non-volatile* constituents, by evaporating *a portion* of the same on platinum foil or in a small porcelain capsule; if the constituents are non-volatile the fixed residuum is subjected to the experiments required in the preliminary examination of solids (tables I. and II.), of course, excepting those which refer to solution.

2. Whether they have *neutral, acid,* or *alkaline* reaction with litmus paper.

The employment of these experiments must never be omitted, since, by careful management, from the results, the presence or absence of whole groups of bodies can be inferred. It is evident that, in a liquid which leaves no residuum on *careful* evaporation (and not even on rapid ebullition), we need not seek for a metallic oxide, which resists the action of fire (fixed base). A *neutral* fluid usually contains only the salts of the alkalies or alkaline earths, since the salts of nearly all the other metallic oxides present an *acid* reaction. A quantity of free alkali present (especially in the absence of non-volatile organic compounds) excludes all oxides which are insoluble in alkaline fluids; if the alkaline reaction is produced here by an alkaline carbonate, the presence of the alkaline earths is also impossible. (The exceptions to this rule are the sesquioxide of iron, alumina, sesquioxide of chromium, protoxide of copper, etc., in the presence of non-volatile organic substances, also oxides which are soluble in cyanide of potassium and in alkaline sulphides, the cyanides, sulphides, etc.). Thus, also, from the presence of certain metallic oxides, the absence of certain acids follows and *vice versâ*; in a reguline metal completely soluble in chlorhydric acid, silver is not looked for, nor is gold, tin, or antimony sought for in one soluble in nitric acid, etc.

One part of the solution of a solid, obtained in the one or the other way, is employed for the detection of *the metallic oxides,* and another for the detection of *the acids.*

A. DETECTION OF THE METALLIC OXIDES.

Table IV. serves as the principal guide for the detection of the metallic oxides, showing in an abstract form the comportment of the same with reagents. With a little reflection, the course, prescribed in this summary, is easily understood. It is indispensable, however, that the following rules be kept in view in the qualitative analysis of compound bodies:

1. *The precipitation, produced by each of the general reagents employed, must be complete.* The precipitant, therefore, is added gradually and as long as a precipitate is produced by it. Moreover, with sulphydric acid, it is known that there is complete precipitation, when the fluid smells strongly of it, *even after being shaken.* Gentle warmth, in almost all cases, promotes the separation of the insoluble compound which has been produced. Some metallic oxides (arsenic acid, molybdic acid, the oxides of platinum, iridium, and rhodium) are but slowly precipitated from liquids saturated with sulphydric acid, often only after being warmed from twelve to twenty-four hours (with arsenic acid it occurs sooner on being heated to 60° or 70° C.)

2. *The precipitates, which indicate the several groups, must be completely freed, by washing with water, from the members of the remaining groups still present in the solution.* This washing is accomplished, according to circumstances, on a filter, or even in a small test tube by continuously allowing the subsidence of the precipitate and pouring off the clear fluid.* When sulphides insoluble in dilute

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* In order to learn whether, after the precipitation of one group, there may still be present the members of one of the other groups,

acids and easily oxidizable are present, some sulphydric acid water is added to the water employed in washing, — in the case of the sulphide of iron or of manganese, some drops of sulphide of ammonium, — so that oxidation from protracted washing is prevented.

Neglect of these two conditions (complete precipitation and washing of the precipitate) causes the members of the various groups to become partially mixed with each other; and in the further prosecution of the analysis, reactions are obtained, to which attention has not been directed in the tables of the separate groups, and which cannot be explained by the unpractised.

3. *The mineral acid which serves for the acidulation of the original solution* (in case it is not sufficiently acid itself) *is chlorhydric or nitric acid,* — either in dilute condition or concentrated, yet not in so large a quantity that the formation of insoluble sulphides should be prevented by them. The former is usually employed, and the possible appearances indicated in table IV. (precipitation of chloride of silver, sub-chloride of mercury, chloride of lead, etc.) are to be considered.

4. If, in the progress of the systematic course of qualitative analysis, one or more members of the different groups, are recognized and proved, as constituents of a substance, by the reagents pointed out in the tables, the analyist (and especially the beginner) must undertake, with the original substance or also with its separate constituents, a course of confirmatory experiments, which may control the results already obtained. These confirmatory experiments should never be neglected by the

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a few drops of the filtrate are cautiously evaporated on platinum foil; if there remain, after ignition, no distinctly perceptible residuum, it is not necessary to pay any further attention to fixed constituents.

beginner for this reason, that it is a principal point in analytical exercises, not only to learn the simple course of analysis, but to become familiar with the comportment of a body in all its relations. Only by following this important rule, will the inexperienced be protected from errors and deceptions. For these arise continually from ignorance of the comportment of bodies, or a non-observance of the conditions, upon which rest the result of an experiment — the appearance of the phenomenon, which we consider as proof of the appearance of a body. In the first and second part of this treatise, the comportment of metallic oxides and acids is treated, for this end, so comprehensively, that we can always find there the material for the confirmatory experiments.

The further discrimination and separation of the metallic oxides is carried on according to tables V., VI., VII., and VIII.; table V. answers for precipitates which are produced in acid solution by sulphydric acid, table VI. for those by *sulphide of ammonium,* table VII. for those by *carbonate of ammonia,* table VIII. for the discrimination and separation of *magnesia* and *the alkalies.*

B. DETECTION OF THE ACIDS OR OF THE BODIES REPRESENTING THEM.

The qualitative analysis of the acids is just as simple as that of the metallic oxides. In almost all cases, the preliminary examination according to tables I. and IX., and the nature of the metallic oxide there pointed out, has specially indicated in which class of acids it is proper to test. The knowledge of the comportment of a salt with solvents, — the reaction of the aqueous solution on vegetable colors, is above all important in this estimate. By igniting a substance alone, as well as by heating it with concentrated sulphuric acid, (according to table IX.,) we ascertain the presence of *organic* or *volatile inorganic* acids. When there is reason to suppose the presence of several acids or their salts in the substance to be examined, the circumstances are to be considered in the previous examination, which might possibly occasion deception; especially since changes may take place on ignition alone or by treatment with sulphuric acid, or other phenomena may arise, which are not produced by each separate acid present. Thus, salts with organic acids are decomposed, when mixed with the nitrates or chlorates, on ignition without any discoloration; with the most a detonation takes place; in presence of a sufficient quantity of organic matter, no *nitrate* can be detected after ignition, but only a carbonate, if the base was an alkali or an alkaline earth. A mixture of a nitrate with a chloride develops, when concentrated sulphuric acid is poured over it, neither pure chlorhydric acid, nor nitric acid, but chlorine and red nitrous acid vapors; in a mixture of a sulphite with a nitrate, (chromate, chlorate, etc.,) the sulphurous acid is converted into sulphuric acid, — most of the sulphides part also with sulphur in such a mixture.

In order not to overlook the presence of volatile organic acids, so far as they may be present in an uncombined condition, the acid solution is neutralized with carbonate of soda, evaporated and ignited; the organic acids will be decomposed with discoloration, whilst without this preparation they would be volatilized undecomposed. For the detection of the more important acids, in the wet way, in the substances to be detected in solution, we follow the plan laid down in tables X. and XI. The use of *general* reagents for acids is only intended, in almost all circumstances, to detect the presence or absence of the members of a whole group of acids. The examination for the separate acids belonging to these groups requires the employment of the special tests given in the tables.

Acid solutions, if the examination for acids must take place in neutral liquids, are neutralized with ammonia, — alkaline solutions with nitric acid, or in circumstances where nitrate of silver cannot be used as a precipitant, with chlorhydric acid. If the compound to be examined was not primarily soluble in water, but was soluble in acids without any visible decomposition, and the base is an alkaline earth or an earth, then the acid solution (as in the case of the phosphates or oxalates of the alkaline earths) cannot be tested, in a neutral condition, by chloride of calcium, since by neutralization with ammonia the whole salt would be precipitated. In such cases, (to which, moreover, attention is directed in the precipitate produced by sulphide of ammonium, while examining the metallic oxides,) the examination of the acids is undertaken in acetic acid solutions (with chloride of calcium for oxalic acid, and with the sesquichloride of iron for phosphoric acid,) or the base is removed first in the proper way, (the alkaline earth by means of sulphuric acid, the heavy metals by means of sulphydric acid or sulphide of ammonium). From the salts of organic acids which are insoluble in water, the acids are removed by boiling with carbonate of soda and the neutralized filtrate is tested with chlorhydric acid. If it is necessary to examine, in a liquid containing sulphydric acid or a soluble sulphide, for such acids as are precipitated in acid solution by the nitrate of silver, but not by the sesquisalts of iron, (as chlorhydric, bromhydric, and iodhydric acid,) the contained sulphur is removed by the addition of sesquisulphate of iron, and the filtrate, being acidulated with nitric acid, is examined for these acids. Compounds that are insoluble in water and in acids are made soluble in order to be examined for acids, according to tables III. and X.

OUTLINES

OF

QUANTITATIVE ANALYSIS.

PART FOURTH.

EXAMPLES FOR PRACTICE IN QUANTITATIVE ANALYSIS.

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1. Sulphate of Copper. ($CuO, SO_3, HO + 4$ aq.)

The protoxide of copper, sulphuric acid, and water are to be estimated. In the estimation of each, from one to two grm. of the pure, air-dried salt is taken.

a. *Protoxide of copper.* — The aqueous solution, while boiling, is precipitated with caustic alkali, filtered and washed with hot water, until the filtrate will not leave a residuum on platinum foil, — then the dried protoxide of copper is ignited after the filter has been burned to ashes by itself on the lid of the crucible. If a portion of the protoxide has been reduced to the metallic condition, it is moistened with a few drops of nitric acid and heated once more to redness, the crucible being covered.*

b. *Sulphuric acid.* — The aqueous solution of the salt, mixed with some chlorhydric acid, is completely precipitated by chloride of barium; the precipitate is boiled for a few minutes with the acid fluid, then allowed to subside and the supernatant liquid to run clear through the filter. The precipitate is stirred with hot water and filtered only when it has been fully deposited. The washed sulphate of baryta is ignited, after the filter has been burned by itself. ($BaO, SO_3 : SO_3 = 116, 5 : 40.$)

c. *Water.* — The pulverized salt is dried at 100° C., whereby it loses four atoms of water; by gentle ignition, the fifth atom (Halhydratwasser, G.) can also be estimated.

2. Sulphate of Iron. ($FeO, SO_3 + 7$ aq.)

a. *Protoxide of Iron.* — A solution of one or two grammes of the pure salt, free from the sesquioxide, with the addition of some chlorhydric acid and chlorate of potassa, (or even nitric acid,) is heated until there is complete oxidation, and then a precipitate is produced with excess of ammonia. The washed sesquioxide of iron is ignited, weighed, and then by calculation, the protoxide is estimated. ($Fe_2O_3 : Fe_2O_2 = 80.72.$)

b. *Sulphuric acid.* — Its estimation is accomplished as in No. 1.

3. Chloride of Sodium. (Na, Cl.)

a. *Chlorine.* — From 0.3 to 0.5 grammes of pure decrepitated common salt is dissolved in water, acidulated

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* It is necessary always to deduct, for the ash of the filter, an equivalent weight, (from 0.001 to 0.004 grm).

with some nitric acid, and the chlorine precipitated by nitrate of silver. By gentle heat and violent agitation the liquid is quickly made clear. The chloride of silver is removed, either by decanting to a porcelain crucible, washed out with warm acidulated water and then fused, or it is filtered off, dried after being washed and freed as much as possible from the filter, evaporated together with the filter-ash and a few drops of aqua regia in a porcelain crucible, then fused and weighed when cold. Or the chloride of silver is filtered, on a filter which has been dried at 110° C, and weighed, (either in a tube or between two watch glasses,) washed out and weighed after it has been dried by itself at the same temperature. ($AgCl : Cl = 143,5 : 35,5$.)

b. *Sodium.*—About one gramme of the salt is heated along with concentrated sulphuric acid, added by degrees, in a weighed platinum crucible, until all the chlorhydric acid is expelled, then heated more strongly, and at last ignited, whilst a small piece of carbonate of ammonia is held in the crucible. From the weight of the neutral sulphate of soda, the sodium is calculated. ($NaO, SO_3 : Na = 71 : 23$.)

4. Calcareous Spar. (CaO, CO_2.)

a. *Lime.*—About one gramme of the compound is dissolved in chlorhydric acid, care being taken that no loss is suffered by the effervescence, saturated with ammonia and the lime precipitated by oxalate of ammonia (or oxalate of potassa); after standing some hours at a gentle heat, the precipitate is filtered off, washed with hot water, dried and gently ignited, whilst the filter is burned by itself on the lid of the crucible. With too strong ignition the carbonate of lime easily loses some of its carbonic acid; when this has happened, which can be recognized by an alkaline reaction of the same, it is moistened with some carbonate of ammonia, evaporated and again gently ignited. ($CaO, CO_2 : CaO = 50 : 28$.)

Or, the moderately dilute chlorhydric acid solution of the calcareous spar is mixed with sulphuric acid and then with a large quantity of alcohol. The precipitated sulphate of lime, being washed with alcohol, is weighed after ignition. ($CaO, SO_3 : CaO = 68 : 28$.)

b. *Carbonic acid.*—About one gramme of the compound is decomposed, in an apparatus prepared for the quantitative estimation of carbonic acid, by moderately concentrated chlorhydric or nitric acid and the loss of weight estimated after the carbonic acid in the apparatus has been replaced by atmospheric air.

5. SULPHATE OF MAGNESIA. ($MgO, SO_3 + 7$ aq.)

a. *Magnesia.*—The air-dried salt is dissolved in water, mixed with chloride of ammonium and ammonia, and the magnesia precipitated by the phosphate of soda. After an exposure of some hours to a gentle heat it is filtered, washed out with water containing ammonia (one part of ammonia and three of water), and the dried precipitate ignited. ($2\,MgO, PO_5 : 2\,MgO = 111 : 40$.)

b. *Sulphuric acid* and *water.*—These are estimated as in No. 1.

6. PHOSPHATE OF SODA. ($2\,NaO, HO, PO_5 + 24$ aq.)

a. *Phosphoric acid.*—The aqueous solution of the fresh uncrystallized air-dried salt, is precipitated by a mixture of sulphate of magnesia, chloride of ammonium, and ammonia,—and the precipitate being washed with water containing ammonia (as in No. 5, a.), is dried and ignited. ($2\,MgO, PO_5 : PO_5 = 111 : 71.$)

b. *Soda.* — The aqueous solution of the salt is mixed with acetate of ammonia, then with the sesquichloride of iron until a reddish color is produced, heated to ebullition, filtered, and washed with hot water. (Or the solution of the salt is precipitated by an excess of sesquichloride of iron, and then with ammonia.) The filtrate is evaporated, gently ignited, and the residuum weighed either as the chloride of sodium, or (after treatment with sulphuric acid, as in No. 3, b.) as the sulphate of soda.

If *a given volume* of a solution of the sesquichloride of iron, containing *a known amount of the sesquioxide*, is employed, then the amount of phosphoric acid is known from the excess of weight of the ignited precipitate.

c. The estimation of the amount of water is accomplished (as in No. 1) by drying at 100° C. and then by ignition.

7. ACETATE OF LEAD. ($PbO, C_4H_3O_3 + 3\,aq.$)

a. *Protoxide of Lead.* — The aqueous solution of the salt is precipitated by carbonate of ammonia with the addition of some free ammonia, and the precipitate, ignited in a porcelain crucible, is weighed as the protoxide of lead, after the filter has been carefully reduced to ashes separately. Or a precipitate is produced with moderately dilute sulphuric acid, which is added in large excess, — the sulphate of lead is washed with water containing sulphuric acid, and finally with alcohol. It is then collected on a filter dried at 120° C. or even ignited after the filter has been carefully burnt alone. Or the compound is converted into sulphate of lead, by evaporation along with sulphuric acid, with the addition of a few drops of nitric acid, and then ignited. ($PbO, SO_3 : PbO = 151,7 : 111,7.$)

b. *Acetic acid.* — The carbon and hydrogen are estimated by an elementary analysis.

8. TARTRATE OF SODA-POTASSA. ($KO, NaO + C_8H_4O_{10} + 8$ aq.)

a. *Potassa* and *Soda.* — The salt is ignited, the charcoal digested in dilute chlorhydric acid (or solution of chloride of ammonium), filtered, evaporated, and the chloride of potassium and of sodium which constitute the residuum, after being gently ignited in a platinum crucible, are weighed. They are then dissolved in a small amount of water, an excess of bichloride of platinum added, evaporated in a water bath to dryness and treated with alcohol, which leaves the double chloride of potassium and platinum behind. It is now filtered on a weighed filter, which has been dried at 100° C. ($KCl, PtCl_2 : KCl : KO = 244,4 : 74,7 : 47,2.$) The quantity of chloride of sodium is found by deducting the chloride of potassium from the weight of the two chlorides, or it is directly estimated, if the double chloride of sodium and platinum is decomposed by evaporation and heating with pure oxalic acid (or in a stream of hydrogen gas) and the aqueous solution of the chloride of sodium, freed from the platinum by filtration, is evaporated.

b. The amount of water is obtained by careful drying, the tartaric acid by the combustion of its carbon and hydrogen by means of the protoxide of copper with the addition of some protophosphate of copper.

9. SULPHATE OF BARYTA. (BaO, SO_3.) SULPHATE OF STRONTIA. (SrO, SO_3.) SULPHATE OF LIME. ($CaO, SO_3, 2\,HO$.)

a. WATER. — The amount of water in gypsum is estimated by ignition.

b. SULPHURIC ACID. — The finely pulverized sulphate of baryta or strontia, is fused in a platinum crucible with four parts of carbonate of soda-potassa (free from sulphuric acid), the mass is extracted by boiling with water and the sulphuric acid is precipitated, from the filtrate saturated with chlorhydric acid, (as in No. 1,) by chloride of barium. Finely pulverized gypsum is wholly decomposed by boiling with a concentrated solution of carbonate of soda.

c. BARYTA (STRONTIA, and LIME). — The carbonate of baryta, being thoroughly washed, is dissolved in dilute chlorhydric acid, and precipitated, while hot, with dilute sulphuric acid. If *strontia* is present, the baryta is precipitated by silico-fluohydric acid, with addition of some alcohol, and the silico-fluoride of barium is weighed on a filter dried at 100° C. ($3\,BaF, 2\,SiF_3) : BaO = 419,1 : 76,5$. The strontia is precipitated, from the filtrate containing alcohol, by dilute sulphuric acid, or it is evaporated along with it to dryness, and the resulting sulphate of strontia then ignited. Baryta can be precipitated, from a dilute neutral solution, by the neutral chromate of potassa, while the strontia remains undissolved.

If *lime* is present, along with baryta, the latter is first thrown down from a very dilute solution by sulphuric acid, and then, after neutralizing with ammonia, the lime by oxalate of ammonia.

Baryta, strontia, and *lime,* are separated, when the carbonates of the earths are carefully converted into dry neutral nitrates, and then digested, in a closed vessel, for a long time in the cold with absolute alcohol; from the filtrate, after the evaporation of the alcohol, the dissolved nitrate of lime is precipitated by oxalate of ammonia; the baryta and strontia are then separated as above.

10. Dolomite. Bitter-spar.

(Carbonate of lime and of magnesia, frequently also proto-carbonate of iron.)

The mineral, dried at 100° C., is dissolved (in a flask or covered beaker glass) in warm chlorhydric acid (with the addition of some nitric acid, or chlorate of potassa), mixed with chloride of ammonium and slight excess of ammonia, the sesquioxide of iron quickly filtered off, and the lime thrown down from the filtrate by oxalate of ammonia (according to No. 4), then the magnesia by phosphate of soda (according to No. 5). If the mineral contains silicic acid, this remains behind on the attempt to dissolve it in acid, and is filtered off. The sesquioxide of iron, precipitated by ammonia, contains some magnesia (if a quantity of carbonate of ammonia was present, some lime also); for exact estimation of the sesquioxide of iron, it is precipitated as in the analysis of spathic iron (No. 11).

The carbonic acid is estimated either directly or it is calculated from the quantity of the oxides obtained.

11. Spathic Iron.

(Contains proto-carbonate of iron, usually also the proto-carbonates of manganese, lime, and magnesia.)

About two or three grammes of the dried, powdered mineral is dissolved in warm chlorhydric acid, with the gradual addition of nitric acid or chlorate of potassa, until there is complete sesquioxidation of the protoxide of iron,—the fluid somewhat diluted is nearly neutralized with carbonate of soda, and then mixed with a saturated solution of acetate of soda, and heated to ebullition, by which means the sesquioxide of iron is alone precipitated, which should be filtered while warm and washed with hot water. ($Fe_2O_3 : 2(FeO, CO_2) = 80 : 116.$)

The filtrate, mixed with hypochlorite of soda in slight excess, is made weakly acid with acetic acid, and suffered to stand twenty-four hours, by which means all the manganese is precipitated as the binoxide.* It is ignited and weighed as Mn_3O_4. ($Mn_3O_4 : 3(MnO, CO_2) = 114,8 : 172,8$). The lime and magnesia are estimated (as in No. 10), in the fluid filtered off from the binoxide of manganese.

Or, from the aforesaid solution of spathic iron, after it has been nearly neutralized with ammonia, the sesquioxide of iron is precipitated by neutral succinate of ammonia (as the sesqui-succinate of iron, which becomes the sesquioxide of iron on ignition in the air), the acidulated filtrate is evaporated to dryness, the ammoniacal salts expelled by ignition, and from the chlorhydric acid solution of the residuum, which has been saturated with chlorine, the manganese is first precipitated by ammonia, after that the lime and magnesia are precipitated as above.

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* If the fluid acquires a red color in consequence of the formation of permanganic acid, a few drops of alcohol are added, and it is only filtered when the fluid becomes again colorless.

12. Copper Pyrites. (Cu_2S, Fe_2S_3.)

The pulverized mineral is gradually dissolved in warm concentrated chlorhydric acid, with the gradual addition of chlorate of potassa, the pure yellow sulphur thus separated, after it is washed and gently dried in a porcelain crucible, is weighed, the sulphuric acid is precipitated from the solution (as in No. 1), by chloride of barium, and the copper, from the fluid freed from baryta by dilute sulphuric acid, by sulphydric acid. The proto-sulphide of copper being quickly filtered and then washed with sulphydric acid water, is dried on the filter and dissolved by concentrated nitric acid in a porcelain capsule (the filter having been first burned and its ashes with the protoxide of copper attached to them being added). The protoxide is thrown down from the clear solution (as in No. 1), by caustic potassa.

The fluid which was filtered off from the protosulphide of copper is then heated, some chlorate of potassa is added for the higher oxidation of the protoxide of iron, and the sesquioxide of iron is precipitated by ammonia.

13. Zinc Blende. ($Zn S$.)

This generally contains iron, and sometimes copper and cadmium.

The mineral is treated, for its solution and the estimation of its sulphur, as copper pyrites (No. 12). From the filtrate (freed from baryta and nearly neutralized), the sesquioxide of iron is precipitated by an alkaline succinate (or less accurately by boiling the liquid mixed with acetate of soda, or by saturation with ammonia), and then the protoxide of zinc, by the use of sulphide of ammonium in fluids containing ammoniacal salts, or carbonate of soda at the point of ebullition, in case ammonia is absent. The sulphide of zinc being washed out, is dissolved (while yet moist and along with the filter) in hot concentrated chlorhydric acid and precipitated, at the point of ebullition, by carbonate of soda. The ignited precipitate is the protoxide of zinc. A slight amount of copper and cadmium is precipitated (before the iron) by sulphydric acid, — the sulphides (along with the filter) are dissolved in nitric acid, saturated with potassa and mixed with cyanhydric acid until there is complete solution. The cadmium is precipitated from this solution by sulphydric acid, and then (after boiling with aqua regia) the copper by potassa (as in No. 1).

The sulphide of cadmium is dissolved in nitric acid, the oxide precipitated by carbonate of soda and ignited after washing.

14. Alloys of Copper and Zinc. (Brass.)

From two to three grammes are dissolved in chlorhydric acid under the gradual addition of nitric acid, it is diluted with water and the copper then precipitated as the protosulphide, which is treated as in No. 12. The filtrate is heated to ebullition, and the protoxide of zinc precipitated by carbonate of soda, after the removal of the sulphydric acid.

Or, the solution of the brass is neutralized by ammonia, solid caustic potassa is added in small excess, and the fluid heated until it becomes colorless and the protoxide of copper then filtered off; the protoxide of zinc is precipitated from the filtrate, after it has been acidulated, as above.

If the brass contains tin, it is dissolved in nitric acid, when the latter as binoxide remains undissolved; if lead be contained, it is precipitated, before the copper, from the solution somewhat evaporated, by dilute sulphuric acid.

15. ALLOYS OF COPPER AND TIN. (Bronze, bell, and cannon metal.)

The alloy, cut into small pieces, is heated along with strong nitric acid, until all the metal is oxidized, most of the acid is then evaporated, diluted with hot water and binoxide of tin filtered off. It is ignited and weighed. ($SnO_2 : Sn = 74 : 58$). The protoxide of copper is precipitated from the filtrate (as in No. 1) by potassa.

If lead, zinc, and iron are present, the first is precipitated, after the removal by filtration of the binoxide of tin, by means of sulphuric acid, then the copper by sulphydric acid; the zinc and iron are separated as in No. 13.

Or, the alloy is dissolved in aqua regia, precipitated by carbonate of soda, and the liquid being heated to ebullition is saturated with nitric acid. After the digestion, the binoxide of tin alone remains undissolved; the metals in solution are then separated as above.

Or, the alloy is heated in dry chlorine gas (in a bulb-tube). The tin (along with the iron) is volatilized as the chloride, which can be caught in dilute chlorhydric acid and the tin precipitated as the sulphide, which is converted into the binoxide by roasting. The chloride of copper (and chloride of lead) are dissolved in nitric acid, after their reduction by hydrogen, and separated in the customary way (vide No. 14).

16. Alloys of Copper, Zinc, and Nickel. (Argentan or German Silver.)

From the solution in nitric acid (or in a nitrate) not holding too much free acid, the copper is first precipitated as the sulphide of copper (No. 12), then, after expelling the sulphydric acid, the nickel and the zinc by carbonate of soda at the point of ebullition. The ignited and triturated oxides, are heated in dry hydrogen gas, as long as any water is formed, and then, from the mixture of metallic nickel and the protoxide of zinc, the latter (by exclusion of air) is abstracted by digestion for twenty-four hours with concentrated carbonate of ammonia.

Or, the concentrated solution of both oxides is mixed with excess of potassa, and then, until there is a clear solution, with cyanhydric acid. Protosulphide of potassium (not sulphide of ammonium) precipitates only the zinc from this solution. After the decomposition of the filtrate by aqua regia, the protoxide of nickel is precipitated by potassa.

17. Alloys of Silver and Copper. (Silver coin.)

The nitric acid solution is precipitated by dilute chlorhydric acid, and the chloride of silver estimated as in No. 3. The copper is precipitated from the filtrate by potassa (as in No. 1). A proportion of gold in the alloy remains as a brown powder when the alloy is dissolved.

18. Alloys of Gold with Silver or Copper. (Coined and manufactured gold.)

Alloys of gold and silver, which contain less than 15 per cent. of silver, give up their gold to aqua regia (precipitable from it by oxalic acid or the proto-sulphate of iron), whilst the chloride of silver alone remains undissolved; if there is 80 per cent. of silver, nitric acid removes all the silver, the gold remaining as residuum (which can be examined, after solution in aqua regia, for any silver that is possibly left back); alloys with from 15 to 80 per cent. of silver are first fused in a porcelain crucible, together with three parts of pure lead and then treated with nitric acid, by which means only the gold is left behind; from this solution, the silver is precipitated by cyanhydric acid, or after considerable dilution, with chlorhydric acid (vide page 58).

Or, the thinly rolled out alloy is heated along with concentrated sulphuric acid, as long as any gas is disengaged, and the sulphate of silver dissolved in hot water is poured off from the gold.

Alloys of gold and copper are dissolved in aqua regia and the gold precipitated by oxalic acid, then the copper by potassa; or the gold is precipitated by sulphate of iron, and the copper by sulphydric acid.

19. Alloys of Tin and Lead. (Solder.)

This analysis is performed according to page 77, by oxidation with moderately strong nitric acid, when the binoxide of tin is left behind, which is filtered off after dilution with water. The filtrate is evaporated, with the addition of some dilute sulphuric acid, until the nitric acid is driven away, diluted then with water and the sulphate of lead filtered off, (No. 7.)

20. ALLOYS OF ANTIMONY AND LEAD. (Type.)

These are oxidized with nitric acid and digested, after saturation by ammonia, with excess of yellow sulphide of ammonium, free from contact with the air. All the black sulphide of lead is filtered off on a weighed filter that has been dried at 120° C., washed with dilute sulphide of ammonium and then with water, and weighed, after being dried. The sulphide of antimony is thrown down from the filtrate by dilute sulphuric acid. It is then either converted into antimoniate of soda (vide page 78)—($NaO, SbO_5 : Sb. = 200 : 129$), and weighed as such, or a determined quantity of the dried and weighed precipitate, after its oxidation by concentrated nitric acid, is dissolved in chlorhydric acid with the addition of chlorate of potassa, and the contained sulphur precipitated, from the dilute solution (mixed with tartaric acid), as the sulphate of baryta. From the quantity of sulphur that of the antimony can be calculated.

In a similar way arsenic is separated from lead, only sulphide of arsenic is changed into arsenic acid by chlorhydric acid and chlorate of potassa, and is estimated (according to page 206), as the arseniate of ammonia-magnesia.

21. ARSENIC, ANTIMONY, AND TIN.

Their quantitative separation is performed according to page 88.

22. COBALT GLANCE. ($CoS_2,CoAs$.)

This usually contains also nickel and iron, and sometimes manganese and gang (Bergart). *Copper-nickel* (Ni_2As), *Cobalt-speis,* and *Nickel-speis* (which often also contain copper or bismuth) and Speis Cobalt ($CoAs_2$), are examined like Cobalt Glance.

a. About three grammes of the mineral, very finely triturated, are carefully mixed with six times their weight of a mixture of two and one half parts of nitre and three parts of carbonate of soda, in a porcelain crucible, then kept in a fused condition for some time at a low red heat, and after partially cooling, treated with water, and filtered, and the oxides thus formed, washed.* The solution contains all the arsenic as arsenic acid, and all the sulphur as sulphuric acid, along with the alkaline carbonate. It is acidulated by chlorhydric acid, and the sulphuric acid (as in No. 1) precipitated with chloride of barium, and weighed as sulphate of baryta. $BaO,SO_3:S=116,5:16$. From the fluid, filtered off from the sulphate of baryta, the excess of baryta is first removed by means of dilute sulphuric acid, the filtrate is then saturated with ammonia and mixed with sulphate of magnesia (and chloride of ammonium). After standing some hours, the precipitate is removed by filtration, washed with dilute ammonia, and dried at 100° C., $[(2\,MgO, NH_4O, AsO_5, HO):As=$

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* If the porcelain crucible, when the contained mass is still at a temperature of from 100° to 120° C., is placed carefully (the upper part first) in a cup of hot water, the contents are dissolved out with ease, without breaking the crucible, which is unavoidable when the same is allowed to get cool.

190:75.] The washed oxides, after the reduction of their filter to ashes, are dissolved by digesting with concentrated chlorhydric acid, and the sesquioxide of iron is first precipitated from the solution (by heating to ebullition the liquid, made as neutral as possible, and mixed with acetate of soda, or by the use of the succinate of soda), then the protoxide of nickel and of cobalt are thrown down, by caustic potassa, at a boiling heat, and are finally separated as on page 36. (If the mixture of both oxides is reduced to the metallic condition in a stream of hydrogen gas, and then weighed, the direct estimation of the cobalt is not necessary.)

If the ore contain copper or bismuth, these should be first precipitated, before the sesquioxide of iron, from the acid solution by means of sulphydric acid; in the filtrate the iron is reconverted into the sesquioxide by heating with some chlorate of potassa.

If the ore contain also manganese, the three oxides (after the precipitation of the sesquioxide of iron) are converted into sulphides (either by the introduction of sulphydric acid into the solution saturated with ammonia, or more precisely by a gentle ignition of the washed oxides present, in a small porcelain vessel, in a stream of sulphydric acid); by treating the precipitated sulphides with dilute acetic acid, or the ignited sulphides with dilute chlorhydric acid, the manganese alone is taken up in solution, which is filtered and then precipitated by carbonate of soda.

If the mineral contains gang (Bergart), the latter remains behind on dissolving the oxides in chlorhydric acid, and is estimated by itself.

b. The oxidation of the very finely ground ore can be effected by careful and gradual heating, (in a platinum crucible the interior of which has been carefully covered with carbonate of soda), along with three parts of triturated chlorate of potassa and three parts of dry carbonate of soda, until finally a quiet fusion is attained. The fused mass is then treated as in a.

c. Or, the mineral is dissolved in concentrated chlorhydric acid with the gradual addition of chlorate of potassa (or of nitric acid), the undissolved sulphur left behind is weighed by itself, the sulphuric acid is thrown down from the solution by chloride of barium, and then (after the removal of the excess of baryta by sulphuric acid), the arsenic is precipitated from the liquid, which has been warmed along with sulphurous acid (until it smells no longer of the acid), by means of sulphydric acid. The sulphide of arsenic, abfiltered after standing twenty-four hours, is dissolved in chlorhydric acid, with the addition of chlorate of potassa, and, as above, determined as $2\,MgO, NH_4O, AsO_5, HO$. The solution of the oxide is then treated as in a.

d. Or, the mineral is decomposed, especially if it contain lead or silver, by means of chlorine gas, as gray copper ore (No. 23).

23. Gray Copper Ore.

$$[4\,(Cu_2S, AgS, FeS, ZnS, HgS) + (SbS_3, AsS_3)].$$

The basic and acid sulphides are represented in different gray copper ores, in various quantities.

The finely powdered mineral is decomposed in a tube supplied with two bulbs (with the bent end discharging upwards in a suitable receiver), by a slow stream of perfectly dry chlorine gas. When the heating effect of the same is over, it is warmed in order to sublime off the volatile chlorides from the non-volatile. *Sulphur, arsenic,* *antimony*, *mercury*, and a portion of *iron*, (also with a strong heat, some zinc,) are volatilized; *copper*, *silver*, *zinc*, and the larger portion of the *iron* remain behind as non-volatile chlorides.

The *volatile* chlorides are taken up by a mixture of dilute chlorhydric acid and tartaric acid, and the solution precipitated, warm, by sulphydric acid. The precipitate, being washed with sulphydric acid, is digested with sulphide of ammonium, and the sulphide of mercury remaining (after being washed, first with dilute sulphide of ammonium, and then with water) is filtered off on a filter dried at 100° C., dried and weighed. The arsenic and antimony are precipitated from the filtrate by dilute sulphuric acid, and separated according to page 85. The iron is precipitated from the solution, containing the tartaric acid, by sulphide of ammonium and weighed as the sesquioxide.

The *non-volatile* chlorides leave behind, on digestion with dilute chlorhydric acid, chloride of silver, which is removed by filtration and estimated as in No. 3. The copper is precipitated from the filtrate by sulphydric acid (No. 12), and then the iron and zinc are separated (according to No. 13).

The amount of *sulphur* is best estimated with a special portion of the ore; the same is oxidized along with three parts of chlorate of potassa and three parts of dry carbonate of soda, by careful heating, and the aqueous extract is precipitated by chloride of barium, after it has been acidulated with chlorhydric acid.

Bournonite, *Ruby Silver*, *Lead ores* (Bleisteine), and other compound minerals similar to Gray Copper ore, are examined in the same way.

24. MESOTYPE. (Natrolite.)

$(NaO, SiO_3 + Al_2O_3, SiO_3 + 2HO.)$

The amount of water is estimated by ignition in a portion of the pulverized mineral dried at 100° C.

A second portion, that has not been ignited, is digested in a porcelain dish along with concentrated chlorhydric acid, until a clear jelly is obtained. This is evaporated in a water bath to complete dryness, the residuum is moistened with a few drops of chlorhydric acid, warmed with water, and the silica removed by filtration. It is washed (until the nitrate of silver no longer makes the water, passing through, turbid), *completely* dried and (enveloped in the filter) ignited.

Alumina (and the sesquioxide of iron) is precipitated from the filtrate by means of ammonia (in small excess), or still better, by carbonate of ammonia or sulphide of ammonium. The alumina is washed with a continuous stream of hot water, dried and ignited.

The fluid filtered off from the alumina is evaporated to dryness, gently ignited after the expulsion of the chloride of ammonium, — the remaining chloride of sodium weighed and the soda estimated from it. $(NaCl : NaO = 58.5 : 31.)$

If the mineral contain the sesquioxide of iron, this is separated from the alumina, before its ignition, by boiling with caustic alkali, and after the acid solution of both has been first heated along with some sulphite of soda. The alkaline solution of the alumina is saturated with chlorhydric acid, then heated to ebullition along with some chlorate of potassa, and the alumina precipitated by carbonate of ammonia or sulphide of ammonium.

The silica obtained in the analysis of a silicate must be tested for its purity, as described on page 183. The precipitated alumina (and sesquioxide of iron), dissolved in chlorhydric acid, dried and again treated with chlorhydric acid, yields a small residuum of silica, which is to be filtered off and added to the larger quantity.

25. PREHNITE.

($2\,CaO,\,SiO_3 + Al_2O_3,\,SiO_3 + HO.$)

The amount of water is estimated, in the finely triturated mineral, by ignition, and the residuum, after ignition, is decomposed by concentrated chlorhydric acid, for the separation of the silicic acid, as in Natrolite. The fluid filtered off from the silicic acid is only slightly saturated with ammonia, the alumina removed by filtration not in contact with the air, and the lime precipitated, from the filtrate, by oxalate of ammonia. The alumina, which contains some silica and lime, is, after the separation of the silicic acid, again precipitated by ammonia (or the sulphide of ammonium) and the filtrate containing the lime added to the larger quantity. A proportion of the sesquioxide of iron is separated from alumina as in No. 24.

The analysis of Stilbite ($CaO,\,SiO_3 + Al_2O_3,\,3\,SiO_3 + 6\,HO$) is conducted in the same way, with this change however, that the non-ignited mineral is decomposed by chlorhydric acid, as in Natrolite and most of the other Zeolites.

26. Olivin. ($3(FeO, MgO) + SiO_3$.)

This generally contains traces of the protoxide of nickel and of manganese, often also copper and tin. It is treated for the separation of the silicic acid as Mesotype (No. 24); the quantity of copper and tin occasionally present, is removed from the solution that has been filtered off from the silicic acid, by sulphydric acid; the sesquioxide of iron is thrown down from the fluid reoxidized (by means of chlorate of potassa), by boiling the nearly neutralized solution along with acetate of soda, or by the succinate of ammonia, then the protoxides of manganese and of nickel are precipitated from the liquid saturated with ammonia, by sulphydric acid, and finally the magnesia by phosphate of soda.

27. Felspar.

($KO, SiO_3 + Al_2O_3, 3SiO_3$.)

a. *Estimation of the silicic acid and alumina* (and sesquioxide of iron).—The very finely triturated and accurately dried mineral is intimately mixed with four times its weight of carbonate of soda-potassa, and fused by subjection to a gradually increasing red heat during a quarter of an hour, the crucible while yet hot is placed on a cold plate of iron, and the mass when cold is then easily separated from the sides of the crucible and gradually saturated, in a covered beaker glass, with chlorhydric acid. After complete decomposition, the silicic acid and alumina are separated (as in No.'s 24 and 25), determined and tested. If the Felspar contains lime, the alumina is precipitated by ammonia, and the lime by oxalate of ammonia.

b. *Estimation of the potassa* (*and soda*). — A second portion of the mineral powder to be examined is decomposed, being drenched with dilute sulphuric acid, in a platinum capsule (vide page 162), by the vapors of fluohydric acid produced in an appropriate apparatus of lead; — after its complete decomposition, it is evaporated to dryness and heated along with concentrated sulphuric acid until all the terfluoride of silicium, and also the excess of sulphuric acid, is driven away. From the solution of the residuum in dilute chlorhydric acid, there is precipitated now the alumina and the sesquioxide of iron (to be separated as in No. 24) by carbonate of ammonia, and the filtrate is evaporated to dryness. After the expulsion of the sulphate of ammonia by careful heating (towards the last, in an atmosphere of carbonate of ammonia, a small piece of this salt being held in the crucible heated to redness), the neutral sulphate of the alkali is weighed.

If a quantity of soda is present it is separated (as in No. 8), by means of the bichloride of platinum with the addition of some chlorhydric acid. The sulphate of potassa and of soda are converted, by prolonged ignition along with chloride of ammonium, into chlorides which are more easily separated.

If it is desired that the whole of the constituents of the mineral shall be estimated in one portion, the decomposition is accomplished by powerful ignition along with four or five times the weight of hydrate of baryta, or carbonate of baryta. After the separation of the silicic acid from the mass immersed in chlorhydric acid, the baryta is first precipitated by dilute sulphuric acid (carefully added).

28. Glass.

(Silicate of lime and potassa or soda, often also protoxide of lead); — containing some of the sesquioxide of iron and of manganese, alumina and magnesia.

The decomposition, and estimation of the alkalies is effected as in Felspar (No. 27). After the separation of the silicic acid, there is first precipitated (after the addition of chlorine water) sesquioxide of iron, and of manganese, and alumina, (together with some magnesia,) by means of ammonia, — then the lime by oxalic acid, and the magnesia by phosphate of soda. The protoxide of lead is precipitated by sulphydric acid, after the removal of the silicic acid by filtration.

29. Augite and Hornblende.

(Silicates of lime, magnesia, and alumina, and the protoxide of iron and of manganese).

The decomposition of the very finely triturated mineral is accomplished by fusion along with carbonate of soda-potassa. The fused mass is decomposed by chlorhydric acid with the addition of some drops of nitric acid, and the silicic acid is separated in the usual way. From the filtrate mixed with chlorine water, alumina, sesquioxide of iron, and sesquioxide of manganese (along with some magnesia), are precipitated by ammonia, — and then from the filtered fluid, lime and magnesia in the usual way.

The precipitate produced by ammonia is dissolved in chlorhydric acid, heated to ebullition, and the sesquioxide of iron and alumina precipitated, from the liquid diluted and cold, by the gradual addition of carbonate of soda (whereby, on account of the double carbonate produced, the protoxide of manganese, magnesia, and lime are taken into solution). The protoxide of manganese is then precipitated by hypochlorite of soda; the remaining oxides are separated in the usual way. The sesquioxide of iron and alumina can also be precipitated by carbonate of baryta.

30. Bone Earth.

(Tribasic phosphate of lime and of magnesia, along with carbonate of lime and fluoride of calcium).

Bone earth, when completely burned white, is dissolved in chlorhydric acid, heated for some time, saturated with ammonia, and the precipitate again dissolved in the smallest possible quantity of chlorhydric acid to which is added some acetate of soda. (Usually traces of the phosphate of the sesquioxide of iron are found at this stage, which are filtered off and estimated; in case of a considerable white precipitate, dilute chlorhydric acid is added until it is redissolved). The lime is precipitated from the solution by oxalate of potassa. The fluid filtered off from the lime is saturated with ammonia, whereby the whole amount of magnesia (together with the phosphoric acid corresponding to it), is precipitated. The rest of the phosphoric acid is precipitated from the filtrate by sulphate of magnesia, (chloride of ammonium, and ammonia).

Or, the bone earth is heated along with from two to three parts of pure metallic tinfoil in moderately strong nitric acid, until it is fully oxidized, then diluted with water and filtered. The excess of weight of the phosphate of tin, over the binoxide of tin, computed from the amount of metal present, is phosphoric acid. The lime and magnesia are estimated in the filtrate in the usual way.

For the estimation of the fluorine, it is dealt with according to page 155, or it is estimated from the lime after the removal of the carbonate and (tribasic) phosphate of lime.

To ascertain the quantity of bone earth in bones, the latter are cleansed, and in small pieces treated with water and dried at 150° C. A portion is employed for the estimation of carbonic acid,— while the rest is reduced to ashes.

31. Ashes.

Salts of potassa, soda, lime, magnesia, and of the sesquioxide of iron (more rarely of the protoxide of manganese), along with carbonic, sulphuric, and phosphoric acid, chlorine (sometimes also bromine, iodine, and fluorine), and silicic acid.

Vegetable or animal substances are charred, and gently ignited in a muffle, without any stirring, until all the carbonaceous matter has disappeared. If the substance (or a part of the same) has been previously dried at 100° C. and weighed, the weight of the ashes represents the quantity of inorganic constituents. The ashes thus obtained are triturated and placed in a stoppered glass bottle.

a. *Carbonic Acid.*—Carbonic acid is estimated in a separate quantity of the ashes (or indeed in that used for ascertaining the silicic acid, etc.) by its expulsion, in a carbonic acid apparatus.

b. *Chlorine.*—A separate quantity of the ashes is decomposed by water, which has been acidulated with some nitric acid, and the chlorine is then precipitated from the acid filtrate, by nitrate of silver, as the chloride of silver.

c. *Silicic acid* and the *remaining constituents.* — A somewhat larger quantity of the ashes (from four to five grammes), is decomposed by an excess of chlorhydric acid and the silicic acid separated in the usual way.* The fluid filtered off from the silicic acid is measured or weighed. In one portion of the same (the weight or volume being known) the sulphuric acid is estimated, by precipitation with the chloride of barium; in another the lime, magnesia, sesquioxide of iron, and the phosphoric acid are estimated; and in a third the alkalies.

If, as is the case with the ashes of seeds, all the bases, or by far the greater portion of them, are present as phosphates, then they are treated exactly as in the analysis of bone earth; first saturated with ammonia and then with acetic acid (residuum = phosphate of sesquioxide of iron, Fe_2O_3, PO_5); the lime is then precipitated by oxalate of potassa; then *a part* of the phosphoric acid, and *all* the magnesia, by the addition of ammonia; and *the rest* of the phosphoric acid by a salt of magnesia. In ashes, which are poor in phosphoric acid, there remains in solution, after this treatment (after the precipitation of the lime by oxalic acid and the following saturation with ammonia), either *a portion* or *the whole* of the magnesia; this remaining

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* If the ashes contain — as is generally the case — some charcoal and sand, these remain behind, undissolved, along with the silicic acid. By protracted boiling with dilute potassa-lye in a platinum capsule, the silicic acid is removed; the charcoal and the sand are collected, by filtration, on a weighed filter; the silicic acid is separated from the alkaline solution by evaporation along with chlorhydric acid.

portion is estimated by precipitation with the phosphate of soda or — if the filtrate is yet to be used for the estimation of the alkalies — with phosphate of ammonia.

If the ashes contain, along with the sesquioxide of iron and phosphoric acid, also the protoxide of manganese, the phosphate of the sesquioxide of iron present, is first estimated (by super-saturation with ammonia and then with acetic acid); a certain volume of a solution of the sesquichloride of iron (affording a known quantity of the sesquioxide), is added to the fluid, filtered off, and the whole heated to ebullition. The weight of the phosphoric acid is learned from the weight of the precipitate (after it has been washed with hot water and ignited), by substracting the previously added sesquioxide of iron, and then adding to the remainder the phosphoric acid which was at first present, as the phosphate of the sesquioxide of iron.

In the filtrate containing all the protoxide of manganese, the lime and magnesia, these oxides are then estimated in the usual way (No. 11). For the estimation of *the alkalies* the solution of the ashes is mixed with oxalic acid, then with excess of ammonia, and — if magnesia is in solution — also with the phosphate of ammonia. The precipitate is washed (with water containing ammonia), — the filtrate, to expel the ammonia, is somewhat evaporated, and then precipitated, while yet hot, with acetate of lead. The excess of the added lead salt, is removed (without filtration) by carbonate of ammonia and some free ammonia. The filtrate is evaporated, the ammoniacal salts expelled by gentle ignition, and the alkalies are weighed as chlorides. Their separation is accomplished as in No. 8.

If the ashes contain *iodine*, this is determined in a separate portion by precipitation with the solution of palladium; the black precipitate (PdI) is, after twelve hours standing, collected on a weighed filter, dried over sulphuric acid and weighed. The amount of fluorine in the ashes of plants cannot be determined.

32. Mineral Water.

(Salt springs, sea water, spring water.)

In the analysis of mineral waters, we must have regard to the following substances:—

a. *Acids* (or *halogens*). — Carbonic acid (free or united with bases), sulphydric acid (free or as soluble sulphides), silicic acid, (boracic acid), sulphuric acid, phosphoric acid, chlorine, bromine, iodine, (fluorine,) nitric acid, and acids of humus (crenic and apocrenic).

b. *Bases.* — Potassa, soda, (lithia,) ammonia, magnesia, lime, (baryta, strontia,) protoxide of iron and of manganese, alumina; there may also be present, in smaller quantities, of the heavy metals, copper, lead, tin, antimony, arsenic, (and in the water of mines, also zinc).

Mineral waters, which, along with free carbonic acid (and the carbonated alkaline earths, dissolved in it), are rich in the chlorides or sulphates, are called *saline sourlings* (salinische Säuerlinge); they give a precipitate when boiled, — the fluid filtered off is *neutral* and contains usually also some lime or magnesia as soluble salts. Alkaline *sourlings* contain in addition, a carbonate of an alkali; they have an alkaline reaction after protracted boiling, and the filtrate contains no soluble salt of lime or magnesia. Mineral waters, which are rich in the proto-carbonate of iron are called *chalybeate*, those containing sulphydric acid, *sulphur waters.*

1. The specific gravity* is estimated in a small flask holding about 100 grammes, and the weight of 50, 100, or 200 c. c. of the water can thus be learned, which weight can then be used in further estimations.

2. *Carbonic acid* (free and combined). A certain volume of water freshly obtained from its source, is added to a mixture of ammonia and chloride of calcium (or chloride of barium);—the precipitate, after it has become crystalline, is filtered, free from contact with air, on a weighed filter, dried at 100° C., after being washed, and the carbonic acid then determined therein. The portion of the precipitate adhering to the flask—after the latter has been washed out—is dissolved in a few drops of chlorhydric acid, again precipitated by ammonia and carbonate of ammonia, and then placed on the same filter, after the precipitate before obtained has been washed. We subtract from the amount of carbonic acid thus obtained (calculated from a certain weight of water) that which is precipitated, in combination with lime, magnesia, and the protoxide of iron, by boiling the water, and which we get in the estimation of these bases, and thus we know the quantity of *free* carbonic acid.

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[*] Prof. G. W. Coakley of the College of St. James, Md., furnishes the translators with the following simple formulæ for obtaining the Sp. Gr. from the degrees of Baumé's Hydrometers:—

For liquids heavier than water, $D = \frac{144}{144 - n}$;

For liquids lighter than water, $D = \frac{144}{144 + (n - 10)} = \frac{144}{134 + n}$;

Where D = the *density*, or specific gravity of the liquid, and n = the *number of degrees* of Baumé's hydrometers. These formulæ will generally be found correct within 0.001.

By boiling the water and receiving the gases disengaged (over quicksilver, or in a tube free from air), we learn, after the carbonic acid has been removed by hydrate of potassa, whether still other gases (oxygen, nitrogen, or carburetted hydrogen), are therein dissolved.

3. **Sulphydric acid* (free and combined). A certain volume (not too small) of the mineral water is mixed with some thin starch paste, and then, from a graduated burette, a solution of iodine in iodide of potassium of a certain strength (No. 37) is added drop by drop, until the color of the blue iodide of starch is brought clearly forth. If the water is alkaline it is neutralized for this experiment with acetic acid (or mixed with chloride of barium); if the water is hot, it must first be allowed to cool free from contact with the air. The quantity of sulphydric acid is calculated from the amount of iodine that has been employed. ($I : SH = 127 : 17$).

4. *The sum total of the fixed ingredients.* — About 200 or 300 grammes of the water is carefully evaporated in a platinum basin to dryness, — the residuum heated at 150° or 200° C. and weighed after cooling.

5. *Chlorine,* (Bromine, and Iodine). — The water acidulated with some nitric acid is precipitated with nitrate of silver, and the chloride of silver estimated (No. 3). The quantity of bromine or iodine is detected and estimated in the mother-liquor, pages 142, 144.

6. *Sulphuric acid.* — The water being acidulated with

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* For the complete removal of the free sulphydric acid of mineral waters, Profs. Wm. B. and R. E. Rogers have originated the method of passing a current of hydrogen (or of carbonic acid, if no sulphide be present) through the water to be analyzed until the gas no longer removes any trace of the acid.

TRANS.

chlorhydric acid, is precipitated by chloride of barium (No. 1).

7. *Carbonate of protoxide of iron, lime,* and of *magnesia,* (protoxide of manganese, and alumina). — A large quantity of water (about 500 or 600 grammes) is boiled in a flask during an hour. After filtering, the washed precipitate is dissolved in chlorhydric acid and the sesquioxide of iron (and alumina) is precipitated by ammonia, the lime by oxalate of potassa, the magnesia by phosphate of soda. (In case of a large proportion of manganese, we proceed as in No. 11).

8. *Silicic acid,* (and the sum total of *sesquioxide of iron,* and *alkaline earths*). — A large quantity of the water, acidulated with chlorhydric acid, is evaporated to dryness, and dissolved in dilute chlorhydric acid, when the silicic acid remains. The sesquioxide of iron and the sum total of the alkaline earths are estimated in the filtrate as mentioned above.

9. *Alkalies.* — The water is boiled down to about one half, in a flask, and mixed with baryta water; — the filtrate is precipitated with carbonate of ammonia and free ammonia, filtered and evaporated to dryness (with the addition of the chloride of ammonium, if no chlorine compounds are present); — the gently ignited residuum is weighed and the potassa and soda separated as in No. 8.

10. *Carbonate of soda* (in alkaline *sourlings*). — The water is boiled for a long time, filtered, and the amount of chlorine estimated in a portion of the filtrate, after it has been acidulated with nitric acid; in another portion, the amount of chlorine is estimated after the former has been acidulated with chlorhydric acid, evaporated to dryness, gently ignited, and again dissolved in water. From the difference in weight of the chloride

of silver the carbonate of soda is calculated. ($AgCl : NaO, CO_2 = 143,5 : 53$).

11. *Lime* and *magnesia* (as soluble salts in saline *sourlings*). — The lime is precipitated as the oxalate, and then the magnesia as a phosphate, from the water, which has been freed (as in 7), from the carbonates of the alkaline earths, by long boiling.

12. A proportion of *Lithia* is sought after in the mother-liquor (vide page 41); *strontia*, *baryta*, also *alumina*, and *protoxide of manganese*, as well as *fluorine*, and *phosphoric acid*, are sought after in the incrustations (Sintern) or ochreous precipitates, which are deposited by *sourlings* on exposure to the air or heat. For the discovery of *ammonia*, a large quantity of the water, acidulated with chlorhydric acid, is evaporated, and the residuum is boiled with excess of potassa-lye, the vapors being caught in chlorhydric acid.

Boracic acid is detected by evaporating the water mixed with some carbonate of soda, acidulating with chlorhydric acid and immersing a piece of turmeric paper (page 157).

Nitric acid is sought after according to page 129.

13. For the detection of a proportion of *arsenic* (copper, lead, tin, and antimony), a large quantity of the ochreous deposit is completely dissolved in chlorhydric acid, boiled with sulphurous acid, and super-saturated with sulphydric acid, or tested for arsenic in Marsh's apparatus.

14. *Organic matter.* — If a proportion of organic matter is present, the residuum, left by the evaporation of the water, becomes brown on strong ignition. For the detection of the acids of humus, the ochreous deposit is boiled several hours with potassa, and the filtrate saturated with acetic acid is mixed with acetate

of the protoxide of copper, whereby apocrenic acid is precipitated; if the fluid filtered from this, gives a new precipitate on being warmed with carbonate of ammonia, then crenic acid is present.

33. ALKALIMETRY.

(Estimation of the amount of potassa, soda, or aqueous solution of ammonia in carbonate or caustic alkali.)

a. *Volumetric Test;* by saturating the weighed alkaline carbonate with dilute sulphuric (or oxalic) acid of known strength. In the preparation of the test acid, about 70 grammes of English sulphuric acid is diluted with 600 grammes of water, and it is determined how much of the cooled mixture (by volume) is necessary, in order to saturate 5.3 grammes ($=\frac{1}{10}$ equiv.) of pure anhydrous carbonate of soda. The freshly ignited carbonate of soda (5.3 grms.) is dissolved in hot water, the solution colored blue with a little tincture of litmus and mixed with the acid, from a dropping glass (the burette), — being added drop by drop towards the last, — until the color of the solution passes over from a wine red to a clear red, and streaks which shall be made with the fluid on litmus paper remain red after drying. The volume of the acid that has been employed is now estimated, and so much water is added to the whole amount of acid that exactly 100 cubic centimetres of this dilute acid will saturate 5.3 grammes of pure carbonate of soda. For example, if 37 cub. cent. had been used, every 37 volumes of this acid must be converted into 100 volumes by the addition of water; the whole acid is then measured, and diluted with the proper amount of water for the calculated volume, and the correctness of the mixture confirmed by a second trial. This test acid, which contains in 1,000 cub. cent. (1 litre) 49 grammes of SO_3, HO (= 1 equiv.), is preserved in a well closed vessel. Or, 63 grammes (= 1 equiv.) of oxalic acid (C_2O_3, 3 HO), purified by recrystallization and dried in the air, is dissolved in water, and diluted (at 17.5° C.) until the quantity of 1,000 cub. cent. is obtained.

100 cub. cent. of either of these test acids contain $\frac{1}{10}$ of an equivalent of the acids, and therefore saturate $\frac{1}{10}$ of an equivalent of a carbonated or caustic alkali; that is,

5.3 grm. of carb. or 3.1 grm. of caustic soda,
6.92 grm. of carb. or 4.72 grm. of caustic potassa,
1.70 grm. of caustic ammonia.

Thus if it is used for saturation in the above way of 5.3 grm. or 3.1 grm. of soda, the quantity of cub. cent. employed in the first case gives the amount of carbonate of soda, and in the second the amount of caustic soda.*

The results are most accurate, if the nearly neutralized onion-red solution of the alkali be heated to ebullition, a slight excess (from 5 to 10 cub. cent.) of the test-acid added, and now by means of the exactly titrited † test-soda (No. 34), applied to the warm fluid, (which has been perfectly freed from carbonic acid, by shaking and suction through a glass tube), this excess is ascertained

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* If the burette contain 50 c. c., and every *division* (space between the graduations) on the same expresses 0.5 cub. cent., then the number of *divisions* employed indicate the percentage, if we take the half of the above quantities, that is 2.65 grms. of carbonate of soda, and 3.46 grms. of carbonate of potassa.

† A *titrited* solution is one of known, uniform strength, and the process of making it is called *titrition*. (Volumetric process.)

TRANS.

and subtracted from the amount of test-acid employed. Since the test-acid and test-soda saturate each other, volume for volume, it is only necessary to subtract the volume of this last from the volume of the test-acid which has been employed. The remainder in cub. cent. gives the amount of alkali in per cent.

b. *By estimation of the carbonic acid.* — The carbonated alkali, from which the amount of water has been first removed by ignition, is decomposed in a carbonic acid apparatus by means of sulphuric acid, and the quantity of the carbonated or caustic alkali computed from the loss of weight. If 6.28 grammes of potash or 4.82 of soda be taken, the number of centigrammes of the disengaged carbonic acid divided by two, gives the per cent. in carbonated alkali. A portion of caustic alkali can be recognized in potash or soda, by the fact that its solution has an alkaline reaction on the addition of excess of chloride of barium.

34. Acidimetry.

The methods of acidimetry rest on the same principle as those of alkalimetry.

a. *Volumetric test.* — For the test-alkali a solution of caustic soda (perfectly free from carbonic acid) is employed, which is so titrited that 100 cub. cent. of the same, exactly saturates 100 cub. cent. of the test-acid (consequently $\frac{1}{10}$ equiv. of any acid).* The acid to be tested is best weighed in multiple quantity and then

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* The test-soda is preserved in a flask, in whose cork a chloride of calcium tube is placed, which is filled with a mixture of Glauber's-salts and caustic lime; the small glass tube opening outwards permits the air to enter freely, whilst its carbonic acid is retained by the mixture.

diluted to an estimated volume; for example, 5 × 49 gram. of sulphuric acid, etc., are mixed with water so as to form a volume of 250 cub. cent. and then 50 cub. cent. thereof are used for each experiment. The acid is colored with a few drops of tincture of litmus, heated and an addition made of the test-soda, with shaking, (and towards the last, most accurately added from a burette graduated in $\frac{1}{10}$ cub. cent.,) until the color suddenly passes from violet to a clear blue. The number of cubic centimetres of test-soda employed, gives directly the amount of percentage of acid.

b. *By estimation of the carbonic acid.*—A certain weight of the hydrated acid is placed in an apparatus prepared for the quantitative estimation of carbonic acid, along with an excess of *pure* bicarbonate of soda, and the quantity of the anhydrous acid present calculated from the weight of the carbonid acid, (whose complete disengagement is effected by heating to 50° or 60° C.). For every equivalent of the acid to be tested, two equivalents of carbonic acid are disengaged (No. 44). If there be taken 0.909 grm. of sulphuric, 1.23 grm. of nitric, 0.83 grm. of chlorhydric, and 1.16 grm. of acetic acid for this estimation, the number of centigrammes, which are found as the loss by the disengagement of the carbonic acid, expresses the amount of percentage of anhydrous acid in the acid. With acids largely diluted, as with vinegar, from forty to sixty times the above weight is employed for this purpose.

35. CHLORIMETRY. (Testing chloride of lime.)

Chloride of lime (bleaching lime) contains hypochlorite of lime, chloride of calcium, and hydrate of lime in varying quantities. Its value depends on its amount of hypochlorite of lime or of chlorine in the mixture which is disengaged with acids. Chlorimetry rests on the estimation of this chlorine.

a. *By means of arsenious acid.* — Fourteen grammes of pure arsenious acid are dissolved in potassa-lye, and this solution is diluted to the volume of a litre (1,000 cub. cent. = 2,000 divisions of a graduated dropping glass). 100 divisions (50 cub. cent.) contain then 0.7 grm. of arsenious acid, which requires 0.5 grm. of chlorine for its conversion into arsenic acid ($AsO_3 : 2\,Cl = 99 : 71$).

Five grammes of chloride of lime are then triturated with water, rinsed into a cylinder and diluted with water to 100 cub. cent. Fifty cub. cent. of the arsenic solution is now diluted with water in a beaker glass, over-saturated with chlorhydric acid, colored blue with a few drops of solution of indigo, and mixed with the shaken chloride of lime solution, by means of a dropping glass, until the blue color has nearly disappeared. A drop of solution of indigo is again added and then the chloride of lime solution by drops, with constant agitation, until the color entirely disappears. In the volume of chloride of lime solution (or in the weight of the chloride of lime) employed, there would be contained 0.5 grm. of chlorine. If, of the solution of chloride of lime, 90 divisions (45 c. c.) of the graduated dropping tube have been employed, then the 5 grm. of chloride of lime contain 1.1 grm. of chlorine; or 100 parts of the chloride of lime contain 22.2 parts of bleaching chlorine. 1,000 cub. cent. of chlorine gas weigh (at 0° C. and 0.76 Meters* atmospheric pressure), 3.1932 grammes.

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* = 29.82 inches of barometer. — TRANS.

b. *By means of protosulphate of iron.*—We dissolve 3.915 grm. of pure protosulphate of iron (precipitated by alcohol) in water, add chlorhydric acid and then (with continued agitation) the above solution of chloride of lime, until there is no more protoxide of iron present, until, indeed, the ferricyanide of potassium (with a solution of which a porcelain dish is sprinkled), is no longer made blue by it. The amount of solution of chloride of lime employed, contains just 0.5 grm. of chlorine. ($2\,[FeO, SO_3, 7\,HO] : Cl = 278 : 35.5$).

This test is employed more accurately if, to the solution of 3.915 grm. of protosulphate of iron dissolved in water and acidulated with chlorhydric acid, there is added a quantity of the chloride of lime (about 2 grm. —consequently 40 cub. cent. of the above solution), insufficient for its sesquioxidation, and this oxidation is completed with a titrited solution of permanganate of potassa. For example, in addition to the use of 2 grammes of chloride of lime, 20 divisions of a solution of the permanganate of potassa have been used, of which 45 divisions will oxidize 1.0 grm. of iron or 4.964 of protosulphate of iron (No. 38),—thus the 2 grm. of chloride of lime have oxidized $3.915 - 2.206 = 1.709$ grm. of the protosulphate of iron. $3.915 : 0.5 = 1.709 : x = 0.218$ grm. of chlorine contained in 2 grm. of chloride of lime.

c. Or, the value of chloride of lime is estimated by means of a solution of iodine and sulphurous acid (according to No. 37, c.).

The calculated quantity of chlorine in chemically pure chloride of lime, amounts to 48.9 per cent.; it however seldom contains two thirds of this quantity.

36. Examination of Binoxide of Manganese.

a. The amount of moisture is estimated by drying at 100° C.

b. about 3 grammes of the very finely pulverized binoxide, along with 7.5 grm. of neutral oxalate of potassa and some water is brought in contact with sulphuric acid (in a carbonic acid apparatus having two flasks), and after complete decomposition, the amount of expelled carbonic acid is ascertained by the loss of weight of the apparatus when cool. From the quantity of carbonic acid contained, the quantity of the binoxide is calculated. ($2\,C\,O_2 : Mn\,O_2 = 44 : 4.36.$)

If exactly 2.98 grm. of the binoxide have been taken, then the percentage of the binoxide would be obtained if the weight of the carbonic acid (in centigrammes) is divided by three.

Good binoxide of manganese is crystalline and furnishes a black powder; after drying, it disengages little or no water.

c. Or, the whole quantity of the chlorine which it can produce, is evolved from a weighed quantity of binoxide of manganese, in a little flask with an exit tube for the gas, by heating along with excess of concentrated chlorhydric acid, — this is then received in milk of lime or dilute soda lye, and the quantity of the bleaching chlorine obtained by the chlorimetric process (No. 36).

d. The most exact method is the volumetric test by means of sulphurous acid and iodine (according to 37, d.).

37. Volumetric methods by means of Iodine and Sulphurous Acid.

These methods depend on the fact that iodine and sulphurous acid in a fluid, which does not contain more of the latter than 0.04 per cent. by weight, are converted (by the absorption of HO) into iodhydric and sulphuric acid. This process is applicable to every body which disengages *chlorine* along with chlorhydric acid. It is conducted into a solution of iodide of potassium, the amount of iodine set free is estimated by dilute sulphurous acid, and the quantity of the material to be estimated, calculated from this. This method requires three test-fluids.

1. An *aqueous solution of iodide of potassium,* containing one gramme of iodide of potassium for every ten cub. cent. (This should not be colored by the addition of pure chlorhydric acid.)

2. A *dilute, hydrated, sulphurous acid* which contains about three parts of anhydrous sulphurous acid in 10,000 parts. (This is prepared by adding a little measure flask of concentrated sulphurous acid, to 20 litres of water, and testing 100 divisions of the burette, (50 cub. cent.) of the mixed fluid, with the normal solution of iodine, after some clear starch-paste has been added. If we have employed T divisions of the iodine solution, before the appearance of the blue color, since the quantity of iodine contained in one division is about 0.0025 grm., we still add $\frac{48}{T}$ times the contents of the little measure flask to the whole proportion of dilute acid; this contains then near 0.03 per cent. of SO_2).

3. *An iodine-test solution.* — Pure iodine (dried over chloride of calcium) to the amount of *g* grammes is

dissolved in a concentrated solution of pure iodide of potassium, and the brown fluid diluted to the volume of $\frac{g}{0.005}$ cub. cent., when a division of the dropping glass is equal to 0.5 cub. cent. Every division then contains 0.0025 grm. of iodine. $g = 5$ grm. gives $\frac{5}{0.005} = 1{,}000$ cub. cent. Iodine constantly contains traces of chlorine; but y times chlorine produces the same effect as $\frac{127.1}{35.5} \times y$ iodine; — the true amount of pure iodine in a division of the burette is best estimated by the volumetric analysis (as in a) of the chromate of potassa. Only a few examples of the numerous applications of this volumetric process are subjoined.

a. *The Chromates.* — All these evolve, when boiled with chlorhydric acid, 3 equiv. of chlorine for 2 equiv. of chromic acid, which separate 3 equiv. of iodine from the solution of iodide of potassium: $2\,CrO_3 + 6\,HCl = Cr_2Cl_3 + 6\,HO + 3\,Cl$. Then 1 equiv. of bichromate of potassa corresponds to 3 equiv. of iodine.

From 0.2 to 0.4 grm. of the salt is placed in a small flask holding from 30 to 40 cub. cent., which is then two thirds filled with fuming chlorhydric acid and the chlorine, disengaged by boiling two or three minutes, is conducted (by means of a tube, which is united with the flask by a vulcanized rubber tube without a ligature) into an inverted retort, with a capacity of about 160 cub. cent., filled with the normal solution of iodide of potassium, and having a wide, bulbous neck for the reception of the fluid poured in from above. In the mouth of the gas-tube there is placed, as a valve, a small glass bulb with a handle closed by fusion. After the completion of the disengagement of the chlorine, the contents of the retort are emptied into a beaker glass, and now by means of a stoppered cylinder as many measures of dilute sulphurous acid are added as will cause the brown color entirely to disappear, and, after the addition of some cub. cent. of thin clear starch paste, it is determined how many divisions of the normal iodine solution shall be required to cause the appearance of the blue color (that is for the oxidation of the excess of sulphurous acid). Let the number of the same be $= t'$; the number of measures of sulphurous acid added (n), the iodine (x) liberated by the chlorine, then still the iodine ($a\,t'$) would be required, if *a* expresses the corrected amount of iodine in a division, which is found out in the same process (see below). It is now estimated how many divisions of the iodine sclution are decolorized by a measure of sulphurous acid. Let their number be $= t$. According to the first process *n* measures of sulphurous acid require $x + a\,t'$; after the second, $n.\,a\,t$, whence $x = a\,(n\,t - t')$. Hence x' the quantity of pure bichromate of potassa in the mixture of the salt employed in the experiment,

$$X' = \frac{K + O + 2\,Cr + 6\,O}{3\,I}\,a\,(n\,t - t').^{*}$$

If bichromate of potassa, purified by repeated recrys-

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[*] For example, let the amount of bichromate of potassa employed be $A = 0.2943$ grm.; the number of measures of sulphurous acid $n = 3$; $t = 103.7$; $t' = 16$ and $a = 0.0025387$ grm. of iodine; then the 3 measures of sulphurous acid require $3 \times (103.7 \times 0.0025387)$ grm. of iodine. But they require also $X + 16 \times 0.0025387$.

From $3\,(103.7 \times 0.0025387) = X + (16 \times 0.0025387)$, it follows, $X = 0.0025387\,((3 \times 103.7) - 16) = 0.74917$ grm. of iodine.

$381.3 : 148.6 = 0.74917 : X' = 0.2919$ grm. That is 0.2943 grm. of the salt employed contains, consequently, 0.2919 grm. (or 99.18 per cent.) of the pure salt.

tallization, and perfectly anhydrous, is employed, we get from the equation,

$$a = \frac{3\,\mathrm{I\,A}}{(\mathrm{K}+\mathrm{O}+2\,\mathrm{Cr}+6\,\mathrm{O})\,(n - t')}$$

the quantity of pure iodine, which corresponds with the impure iodine contained in one division, if A indicates the quantity of the bichromate of potassa.

b. *Iodine.* — A few decigrammes of iodine to be tested are dissolved in the iodide-of-potassium liquid (about 0.1 grm. of iodine to 4 or 5 cub. cent. of the liquid), then dilute sulphurous acid (as given above) is added until the brown color disappears, and after the addition of the solution of starch, estimate the excess of sulphurous acid. $a\,(n\,t - t')$ is the iodine contained in the mixture A, employed.

c. *Chlorine.* — The amount of chlorine x, in the experiment, is calculated from the amount of iodine set free, by the equation

$$x = \frac{\mathrm{Cl}}{\mathrm{I}}\,a\,(n\,t - t').$$

For the estimation of chlorine (as in chloride of lime) the solution of the weight A, is placed in an excess of the iodide-of-potassium solution, chlorhydric acid is added until there is a weak acid reaction, and the free iodine is then estimated. From the equation, $2\,\mathrm{I} : 2\,\mathrm{Cl} = a\,(n\,t - t') : x$, is obtained the chlorine contained in A.

$$x = \frac{\mathrm{Cl}}{\mathrm{I}}\,a\,(n\,t - t').$$

If we employ $\frac{100\,\mathrm{Cl}}{\mathrm{I}}\,a$ of dry chloride of lime for the test, then the difference $n\,t - t'$ gives directly the amount per cent.

d. *Superoxides.* — The superoxide is heated along with excess of chlorhydric acid (as in a), and the disengaged chlorine is conducted into an excess of iodide-of-potassium solution. For every equivalent of $R O_2$, one equiv. of iodine is set free. In testing binoxide of manganese, A, the per cent. of the binoxide (x) is obtained by the formula,

$$X = \frac{100\,(Mn + O_2)}{A I}\,a(n t - t').$$

e. *Sulphurous acid* (and *Sulphydric acid*). — The solutions, if they are to be estimated by means of iodine, should contain, at most, only 0.04 per cent. A concentrated acid is diluted in a graduated vessel, with water that has been boiled, and cooled out of contact with the air, nearly to this percentage. From the whole volume P, there we measure off a portion p, mix with starch paste, and then ascertain the requisite amount of the iodine-mixture, a t, for the appearance of the blue color. The acid contained in the vol. P, is

$$X = \frac{P\,(S + O_2)}{P I}\,a t.$$

With sulphydric acid, $S + H$ takes the place of sulphurous acid $(S + O_2)$ in the formula.

38. Testing of Iron.

a. First there is prepared a titrited solution of the permanganate of potassa; then one gramme of fine piano wire, is dissolved in from 25 to 30 grammes of strong chlorhydric acid, (kept as free as possible from contact with the air,) and to this latter solution diluted so as to make one litre (which should contain the iron only as a protoxide), there is added the solution of the permanganate of potassa* from a graduated burette (adding by drops towards the last), until the purple-red color of the fallen drops, on stirring, no longer disappears, and the fluid has become a light rose-red. The number of cubic centimetres of the solution of permanganate of potassa, which has been employed, corresponds to the weight (1 grm.) of metallic iron dissolved. For testing iron ores, these are brought perfectly into solution by digestion along with concentrated chlorhydric acid, and the sesquioxide of iron that may be present is reduced by heating with zinc that is free from iron, until the fluid has become a bluish-green, or less completely by boiling with sulphite of soda, the excess of the sulphurous acid being at last completely expelled. After the reduction, the *acid* fluid is diluted to the volume of about one litre, tested with the titrited solution of permanganate of potassa, and the amount of iron reckoned from the quantity of this solution employed.

39. Testing of Nitre.

a. Six equivalents (168 parts) of iron, which exists as proto-chloride in solution, require for their complete conversion into the sesquichloride one equivalent (102 parts) of nitre. ($6\,FeCl + KO, NO_5 + 4\,HCl = 4\,HO + KCl + NO_2 + 3\,Fe_2Cl_3$.) If less nitre is employed (or

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* The solution of the permanganate of potassa is obtained, for this purpose, by gentle ignition in a hessian crucible of 8 parts of finely triturated binoxide of manganese, 10 parts of hydrate of potassa, and 7 parts of chlorate of potassa (which has been previously stirred with a little water and then evaporated to dryness). The mass fused together is dissolved in hot water, the solution is mixed with a little nitric acid and decanted (not filtered).

if it is impure), there remains a corresponding quantity of the proto-chloride in solution. On this rests the testing of nitre. Two grammes of piano wire are dissolved, in a flask containing about 150 cub. cent., in from 80 to 100 grms. of concentrated chlorhydric acid, kept as free from contact with the air as possible, then 1.2 grm. of the nitre to be tested are added, and it is heated to ebullition until the fluid has again become clear. This is then diluted to the volume of a litre, and the amount of iron present as the proto-chloride estimated by means of a titrited solution of permanganate of potassa, from which the purity of the nitre is calculated. For example, if 50 cub. cent. of the solution of permanganate of potassa are required for the oxidation of 1 grm. of iron, and only 10 cub. cent. have been used in the experiment, then 0.200 grm. of iron are present as the protoxide, which must be subtracted from the 2 grms. employed. 1.2 grm. of nitre have then converted 1.8 grm. of iron into the sesquioxide; but 1.000 grm. of iron requires 0.608 grm. of pure nitre, consequently there was $1.8 \times 0.608 = 1.094$ grms. or since 1.2 grm. of *crude* nitre was taken, 91.2 per cent. of *pure* nitre present.

b. Or, the nitre is converted, by ignition along with half its weight of pine-soot or lampblack (Kienruss), and six times its weight of decrepitated chloride of sodium, into the carbonate of potassa, the amount of potassa estimated alkalimetrically (as in No. 33), and the pure nitre estimated from this.

40. GUNPOWDER.

The hygroscopic water is estimated by drying over sulphuric acid in a vacuum; the amount of nitre is found by extracting with water, evaporating the saline solution, and weighing the strictly dried residuum. For the estimation of the sulphur, one gramme of gunpowder is mixed with an equal weight of dry carbonate of soda, as much nitre, and four times the weight of decrepitated chloride of sodium, and heated in a platinum crucible until the mass has become white. From the solution, the sulphuric acid is precipitated (as in No. 1), by chloride of barium. The loss gives the amount of charcoal.

41. Cyanhydric Acid.

(Bitter-almond water, cyanide of potassium.)

For estimating the officinal cyanhydric acid, a weighed quantity is precipitated with the nitrate of silver until the odor has disappeared, and then the cyanide of silver, washed and dried at 120° is weighed. Bitter-almond and wild-cherry water must first be mixed with ammonia, then with nitrate of silver, and finally with nitric acid. ($AgCy : CyH = 134 : 27$.)

Or, the fluid containing the cyanhydric acid is mixed with a few drops of a solution of chloride of sodium, then with caustic potassa until there is a strong alkaline reaction, and a titrited solution of neutral nitrate of silver added, until the turbidness produced on shaking no longer disappears. ($AgO, NO_5 : 2\,CyH = 170 : 54 = 6.296 : 2$.) If 6.3 grm. of fused nitrate of silver is dissolved in so much water that the volume amounts to 1,000 cub. cent., this then corresponds to 2 grm. of cyanhydric acid (1 cub. cent. to 0.002 grm.).

42. Sugar, Starch.

The estimation of sugar (in diabetic urine, in beets, and in the juice of the grape), is effected by an alkaline solution of the protosulphate of copper, which is obtained by mixing a solution of 40 grammes of crystallized sulphate of copper in 160 grm. of water, with another solution of 160 grammes of neutral tartrate of potassa, in a little water, and from 600 to 700 grm. of caustic soda-lye of the Sp. Gr. of 1.12. The mixture is diluted until it makes 1154.4 cub. cent. Now 10 cub. cent. of this copper solution correspond with 0.050 grm. of dry grape sugar ($C_{12}H_{12}O_{12}$).

In testing a fluid containing sugar, a certain weight is diluted to 10 or 20 times its volume, so that it contains at most, but 1 per cent. of sugar, (for example, 10 cub. cent. are diluted so as to make 200 cub. cent.). On the other hand, 10 cub. cent. of the copper solution are diluted with 40 cub. cent. of water, heated to ebullition, and then the solution of sugar is poured from the graduated burette (by drops towards the last), into the fluid kept boiling, until all the copper is exactly reduced. The nearer this point is attained, so much the more abundant and reddish is the precipitate (the suboxide of copper). A test can be employed to see whether the filtrate furnishes the reactions of copper to sulphydric acid, or, after acidulating, to the ferrocyanide of potassium; with an excess of sugar, the filtrate is yellowish.

In order to estimate beet sugar or starch in this way, they must be converted into grape sugar by heating several hours along with sulphuric or tartaric acid.

100 parts of grape sugar ($C_{12}H_{12}O_{12}$) correspond with 95 parts of beet sugar ($C_{12}H_{11}O_{11}$), and 90 parts of starch ($C_{12}H_{10}O_{10}$).

43. QUININ. (In Cinchona bark.)

About 8 or 10 grammes of the finely pulverized bark is boiled repeatedly with water, to which some chlorhydric acid has been added, and then the bark is washed out with water. The filtrate is evaporated to dryness in a water bath, and the residuum treated with water containing chlorhydric acid, when the cinchona-red is left behind. The filtered solution is concentrated by evaporation, and the impure quinin precipitated by ammonia. It is washed with some water and weighed on a filter dried at 100° C. The quinin can be extracted from it by ether, in which cinchonin is insoluble.

The amount of cinchonin is estimated in commercial sulphate of quinin, by shaking the salt with ammonia, and then with ether. The separated cinchonin is treated with ether for some time, and then weighed as above.

44. MORPHIN. (In Opium.)

About 6 or 8 grammes of opium are extracted repeatedly with hot, dilute alcohol, evaporated (with the addition of 3 or 4 grm. of crystallized carbonate of soda) to dryness, the residuum then washed with cold water, and at last several times with some alcohol; the impure morphin is then dissolved in dilute acetic acid and precipitated from the filtrate by ammonia, which is added only in slight excess. It is weighed on a filter dried at 100° C.

45. Nicotin. (In Tobacco.)

About 10 grammes of pulverized tobacco are exhausted, in an ether extraction apparatus, by ether containing some ammonia, the extract is evaporated so as to drive off the ammonia, the residuum is then neutralized with dilute sulphuric acid containing a known quantity of acid; $(SO_3 : C_{20}H_{14}N_2 = 40 : 162)$.

46. Analysis of Milk.

About 15 or 20 grammes of milk are evaporated to dryness, in a water bath, with a weighed quantity (about 3 or 4 grm.) of gypsum that has been calcined, moistened, and again dried. By weighing, we get the whole weight of the non-volatile constituents (and consequently the amount of water). A weighed portion of the pulverized residuum is repeatedly treated with ether; by weighing *its* dried residuum, we get the quantity of butter (in the loss of weight). This is now treated repeatedly with alcohol (sp. gr. 0.85) and again weighed, — the loss of weight denotes the quantity of milk-sugar and salts soluble in alcohol. If the weight of the added gypsum is now subtracted from the weight of the residuum, we get the quantity of the caseine and insoluble salts.

For the estimation of the incombustible salts, another portion of the milk is evaporated and the residuum ignited, until all the carbon has been burned; their exact analysis is then conducted as that of an ash, (No. 31). For directly ascertaining the milk-sugar, about 50 or 60 grm. of milk are mixed with some acetic acid, heated to 50° or 60° C., filtered, and then the whey, thus prepared, is employed for the estimation of the sugar along with an alkaline solution of sulphate of copper (page 239) which had been previously titrited with pure milk-sugar.

47. Analysis of Urine.

1. The Sp. gravity is determined.

2. The whole weight of *the organic material* dissolved in the urine, and of *the incombustible salts* (and also that of the water), is obtained by evaporating about 15 or 20 grm. of urine, and weighing the residuum when dried at 110° C.; this residuum is ignited in a porcelain crucible, being moistened with some nitric acid, until all the carbon disappears, when the quantity of incombustible salts is obtained. Their closer analysis* is accomplished as that of an ash (No. 31).

3. *Uric acid.*—A large quantity of urine (about 200 grm.) is acidulated with chlorhydric acid, and the uric acid subsiding, after two days, is brought upon a weighed filter; or the dilute chlorhydric acid is mixed with the residuum of urine (from the determination of urea) which is not soluble in alcohol, and the uric acid remaining undissolved is then placed on the filter.

4. *Chloride of Sodium* and *Urea* ($C_2H_4N_2O_2 = U$). a. *Chloride of Sodium.*—A dilute solution of proto-nitrate of mercury gives a precipitate in neutral or slightly acid solutions of urea ($\overset{+}{U}, NO_5 + 4\,HgO$). The proto-chloride of mercury produces no precipitate; if a solution of urea contains chloride of sodium, no precipitate will be produced by the proto-nitrate of mercury, so long as any of the undecomposed chloride of sodium

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* See page 248.

is present ($HgO, NO_5 + NaCl = HgCl + NaO, NO_5$). Each equivalent of mercury corresponds with 1 equiv. of chlorine.

First there is prepared a solution of chloride of sodium of known strength. A cold saturated solution of rock-salt contains 3.184 grm. of salt in 10 cub. cent. If 20 cub. cent. of this solution are diluted with water so as to make 318.4 cub. cent., a fluid is obtained, 10 cub. cent. of which contain 200 millegrammes of chloride of sodium. The normal solution of mercury is exhibited, when crystallized subnitrate of mercury is completely oxidized by nitric acid, evaporated to a syrup and then dissolved in 10 times its volume of water. In order to give the necessary dilution to the same, 10 cub. cent. of the above chloride of sodium solution is mixed with 3 cub. cent. of a solution of urea (containing 4 grm. of urea in 100 cub. cent.), and 5 cub. cent. of a cold saturated solution of sulphate of soda (free from chlorine).* The mercury solution is now added from a burette. If 8 cub. cent. of it are used before the occurrence of a clear and persistent precipitation, it is too much concentrated to allow of an accurate estimation; it is then diluted with its own volume of water, and the experiment is repeated; if now 15.8 cub. cent. are required, then for 158 volumes, 200 must be produced by dilution: 1 cub. cent. corresponds then with 10 millegrammes of chloride of sodium. (If the mercury-solution contain foreign metals, an opalescent effect is produced in the beginning, which is not noticeable on further addition.)

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[*] This is intended to remove the nitric acid which may be disengaged; there is then produced NaO, NO_5 and $NaO, 2\ SO_3$.

A mixture of 2 volumes of cold saturated baryta water, and 1 volume of a saturated solution of nitrate of baryta (free from the chloride and from hyposulphurous acid), serves for the precipitation of the phosphates and sulphates in urine. One volume of this mixture is added to 2 vols. of urine, the precipitate is removed by filtration, the alkaline filtrate is neutralized with some drops of nitric acid, and 15 cub. cent. of this (= 10 cub. cent. of urine), is examined as above. If, for example, 12.5 cub. cent. of the mercury solution is used, these indicate 125 millegrammes of chloride of sodium. In order later to determine urea, the chlorine is precipitated, in all very exact experiments, by the silver solution. 11.604 grm. of fused nitrate of silver are dissolved so as to make a volume of 400 cub. cent. 1 cub. cent. of this solution then precipitates exactly 10 millegrammes of Na Cl. Accordingly in a new examination of the neutral urine containing baryta, there is added exactly as many cub. cent. of the solution of silver, as must be added of the mercury solution, and the urea in the filtrate (free from silver) is estimated as in b. 1.*

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* *Ascertaining the amount of a solution of proto-nitrate of mercury.*—Phosphate of soda is precipitated by the proto-nitrate of mercury, the addition of chloride of sodium causes the precipitate to disappear, inasmuch as the phosphate of soda is not precipitated by the proto-chloride of mercury. An equivalent of chloride of sodium corresponds to an equivalent of protoxide of mercury ($NaCl : HgO = 58.5 : 108$). 20 cub. cent. of a cold saturated solution of chloride of sodium are diluted to the volume of 586.8 cub. cent. by the addition of water. This contains 2 × 3184 milligr. of Na Cl. 10 cub. cent. contain 108.52 milligr. of Na Cl, and correspond to 200 milligr. of protoxide of mercury. To these 10 cub. cent. add 4 cub. cent. of a cold saturated solution of common phosphate of soda (free from chlorine), and add by drops the mercury solution until a persistent precipitate is pro-

b. *Urea.* — 1. *Estimation by titrition.* — This depends on the precipitability of urea by the proto-nitrate of mercury, if the nitric acid set free is removed by carbonate of soda or baryta-water. As soon as the fluid over the precipitate contains mercury, all the urea is precipitated.

100 millegr. of urea require for their precipitation 720 millegr. of protoxide of mercury; therewith on the addition of carbonate of soda, a yellow color appears (the indication of the end of the test). 772 of the protoxide of mercury are necessary for 100 of urea.

10 cub. cent. of the normal mercury solution for the estimation of urea should correspond to 100 millegrm. of urea, and hence must contain 772 millegrm. of protoxide of mercury. The mercury solution is prepared either by converting 100 grm. of mercury into the proto-nitrate, and making, by dilution, a volume of 1400 cub. cent.; or, according to the experiment described on page 244 (note), a concentrated mercury solution is so titrited that 10 cub. cent. of the same, corresponds with somewhat more than 38.5 cub. cent. of

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duced. If, for example, 5 cub. cent. have been employed for this, then it is diluted with an equal volume of water, in order to procure an accurate result, — and we take 10 cub. cent. of the thus diluted solution, add the phosphate of soda and then *instantly* the chloride-of-sodium solution from the burette (very cautiously towards the last, and with continued agitation) until the precipitate is exactly redissolved. If, for example, 12.5 cub. cent. of the chloride-of-sodium solution are used for this purpose, then (in order to control the result), 12.5 cub. cent. of chloride-of-sodium solution are mixed with phosphate of soda, and with mercury solution until the precipitate remains; if now, e. g. 10.25 of mercury solution are necessary, then in the mean 12.5 c. c. chloride-of-sodium solution correspond to 10.12 c. c. mercury solution (containing 250 millegr. protoxide of mercury).

the chloride-of-sodium solution, and consequently contains more than 772 millegrm. of the protoxide of mercury.

The nearly correct normal mercury solution is now correctly titrited with a solution of urea, which contains 4 grm. of urea in 200 cub. cent. To 10 cub. cent. of this (= 200 millegrm. of $\overset{+}{U}$), the mercury solution is added from a burette, until a test of the mixture — when it is mixed on a watch glass, with carbonate of soda — shows a clear yellow color. If 19.25 cub. cent. were necessary for this, then must every 192.5 volumes of the solution be made 200 volumes by the addition of water. A new test must afford the yellow color on the use of 20 cub. cent.

To 2 volumes of urine there is added one volume of the baryta solution mentioned above, and 15 cub. cent. of the filtrate is experimented with, as stated, without adding acid. In order to set aside the influence of chloride of sodium in the urine, which gives the amount of urea too high, there is either subtracted 2 cub. cent. from the amount of cub. cent. employed of the mercury solution, or the amount of chlorine is removed (in very exact experiments), by a titrited solution of silver (according to a, page 244). Chloride of sodium and urea cannot be estimated in the same, but always require two different portions of urine.

In case of an increase of the urea, there is an error which causes the same to prove too little; with its decrease the opposite is the case; on this account, for every 2 cub. cent. which are required over 30 cub. cent., there is added, before the final test with the carbonate of soda, 1 cub. cent. of water. For every 5 cub. cent. which are used less than 30 cub. cent. there is subtracted at the end 0.1 cub. cent. from the sum. For example, if 25 cub. cent. of mercury solution have been necessary, then we count only 24.9 cub. cent. = 249 millegrm. of urea.

2. *As nitrate of urea.*—From 10 to 15 grm. of urine is evaporated to a syrup; this is extracted by alcohol, and the alcoholic extract again evaporated, and mixed, when cooled, with double its volume of colorless nitric acid, whilst the mixture is refrigerated. After some hours the nitrate of urea is placed on a weighed filter, washed out with some nitric acid, pressed between tissue paper, and dried at 100° C. ($C_2H_4N_2O_2, HO, NO_5 : C_2H_4N_2O_2 = 123 : 60$.)

3. *As chloride of platinum-ammonium.* — About 6 or 8 grammes of urine are evaporated with half their volume of concentrated sulphuric acid, heated (about to 200° C.) until no more disengagement of gas takes place, diluted with water, filtered, and then the evaporated wine-yellow filtrate, mixed with some chlorhydric acid, an excess of bichloride of platinum and alcohol containing ether. After standing for some hours, the precipitated chloride of platinum-ammonium is placed on a weighed filter, washed out with alcohol containing ether, and dried at 100° C. [$2 (NH_4Cl, PtCl_2) : C_2N_2H_4O_2 = 446.4 : 60$.] The precipitate can also be ignited and the urea calculated from the amount of metallic platinum.

If the urine contain salts of ammonia and potassa, these are precipitated by themselves (by means of bichloride of platinum and alcohol), and the amount of chloride of platinum-ammonium (or of platinum) obtained is deducted from the above.

4. *As carbonate of baryta.* — A known weight of urea (previously precipitated by a concentrated solution of chloride of barium containing ammonia)— about 30

or 40 grm. — with (about 3 grm.) pure chloride of barium, is heated for some hours, to 220° or 240° C., in a strong glass tube, closed by fusion and placed in an oil bath, and then the weight of the carbonate of baryta that has been formed (and washed out with water free from carbonic acid) is estimated, [$2 (BaO, Co_2) : C_2N_2H_4O_2 = 197 : 60$].

A probable proportion of sugar in the urine is estimated according to page 233; a quantity of albumen is estimated by heating the urine (mixed with a few drops of acetic acid), and filtering off the coagulated albumen. For the detection of lactic acid in the urine, we proceed as on page 177.

NOTE. — A method for the determination of phosphoric acid in urine, founded upon the *insolubility* of the phosphate of sesquioxide of iron, and the *solubility* of the sesquioxide itself in neutral or acetic acid water, was suggested by Professor Liebig, and has been successfully practised. To the urine acetate of soda is first added, and then a titrited solution of sesquichloride of iron; when the iron is in excess, a paper moistened with ferrocyanide of potassium will give a blue reaction with a drop of the urine.

Urine, or $PO_5 + 3 (NaO, \overline{A}) + Fe_2Cl_3 = Fe_2O_3, PO_5 + 3 NaCl + 3 \overline{A}$. — TRANS.

TABLES

FOR

QUALITATIVE CHEMICAL ANALYSIS.

BY

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OF GIESSEN GERMANY.

THIRD EDITION.

TRANSLATED BY

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TABLES.

I. BEHAVIOR OF INORGANIC SUBSTANCES AND THEIR COMPOUNDS IN EXPERIMENTS FOR PRELIMINARY TESTING.

1. *Easily volatile when heated upon charcoal, (or upon platinum foil, or in a dry test-tube)*: —	Compounds of *ammonia* and *mercury*, a few compounds of *arsenic*, *sulphur* and its acids, *water*, etc. Carbon burnt by ignition in the air; all *organic* compounds decompose when heated, most of them separating carbon (and blackening).
2. *Fusible without volatilizing and without changing color*: —	The greater part of the *salts of the alkalies* and several *alkaline earths*. After exposure to a high temperature in the reducing flame, they color turmeric paper brown. Many *silicates*, as Zeolites, Borates, and Alum, puff up. Common salt decrepitates. Of the reguline METALS, *antimony, lead, cadmium, tellurium, bismuth,* and *zinc* are easily fusible before the blowpipe. *Silver, copper,* and *gold* with more difficulty; the former metals give incrustations, (see below 8).
3. *Decrepitate when heated upon charcoal*: —	Nitrates, Chlorates, Perchlorates, Iodates, Bromates, etc.
4. *Infusible, or nearly so, without change of color*: —	The earths and their salts. The alkaline earths and their salts. When heated they phosphoresce with white light. After ignition the earths show no alkaline reaction. Silica, and many of its compounds. Of the reguline Metals, the following are infusible. Iron, nickel, cobalt, molybdenum, tungsten, platinum, iridium, palladium, and rhodium.
5. *Assuming a darker color when heated*: —	Many metallic oxides and their salts, as oxide of zinc yellow (phosphoresces with yellowish-green light). Oxide of tin, titanic acid, pelopic acid, niobic acid, and antimonic acid yellow. Oxide of lead, teroxide of bismuth, oxide of mercury, chromates, etc., brown.
6. *Color the outer point of the blue flame of the blowpipe (upon platinum wire, or, in the case of metallic compounds, upon coal)*: —	**Yellow.** *Soda*, or a mixture of the alkali salts. **Violet.** *Potassa*, (except borate and phosphate of potassa). **Crimson.** *Lithia*, *Strontia.** **Orange.** *Lime.** **Greenish-yellow.** *Baryta,** *Molybdic Acid.* **Green.** *Oxide of Copper*, *Phosphoric Acid*,† *Boracic Acid*,† *Tellurous Acid.* **Blue.** *Arsenic*, *Antimony*, *Lead*, *Silenium*, *Chloride of Copper.* * Transitory, especially when moistened with chlorhydric acid. † In the salts, after moistening with sulphuric acid.
7. *Give, when moistened with a solution of cobalt and strongly heated upon charcoal*: —	**Blue Glass.** *Phosphates*, *Borates*, *Silicates*, } of the Alkalies. **Blue Infusible Mass.** *Alumina* and many of its compounds, *Phosphates* of the *earths*, *Silicic Acid* and some *Silicates* of the *earths.* **Green Mass.** *Oxide of Zinc*, *Titanic Acid*, } Yellowish green. *Binoxide of Tin*, Bluish-green. *Antimonic Acid*, *Niobic Acid*, } Muddy-green. **Flesh-red Mass.** *Magnesia*, *Tantallic Acid.* **Brown or Brick-red Mass.** *Baryta.* **Gray Mass.** *Glucina*, *Lime*, *Strontia*, *Pelopic Acid.*
8. *When ignited with soda (or soda and cyanide of potassium) in the reducing flame, upon charcoal, give*: —	**Garlic Odor.** *Most of the compounds of Arsenic.* **Hepar.*** All *compounds* of *sulphur* (seleninm, tellurium) *without exception.* **Metallic Grains without Incrustation.** Shining ductile scales. *Tin*, white. *Silver*, white. *Copper*, red. *Gold*, yellow. Gray infusible powder. *Nickel*, *Cobalt*, *Iron*, *Molybdenum*, *Tungsten*, *Platinum*, *Iridium*, **Metallic Grains with Incrustation.** *Antimony.* M. brittle, I. white. *Bismuth.* M. brittle, I. brownish-yellow. *Lead.* M. malleable, I. yellow. **Incrustation without Metallic Grains.** *Zinc*, white in the outer flame, not volatile. *Cadmium*, dark-red. *Tellurium*, white. * The substance when moistened blackens silver, and with acids, develops sulphuretted (selenietted or telluretted) hydrogen.
9. *When heated in a glass tube open at both ends, and held obliquely, give*: —	**Odorous Gases.** *Metallic Sulphides*, — of burning sulphur. " *Selenides*, — of putrified radishes. " *Arsenides*, — of garlic. Some *ammoniacal compounds* of ammonia. *Metallic fluorides* (upon addition of phosphate of ammonia-soda). **Metallic Coating.** Some *Arsenides.* Some *compounds* of *Mercury* (especially with soda). **White Coating.** *Arsenides*, crystalline. *Antimonides* *Tellurides* } fusible. Sulphide of lead. Many *salts* of *ammonia.* **Fused Sublimate.** Higher *sulphides*, brownish-yellow. *Selenides* and selenium, reddish-black. (Also sulphide of arsenic). **Drops of Water.** *All hydrates*, (more distinct in a flask).
10. *In contact with zinc and chlorhydric or sulphuric acid color the fluid*: —	**Violet or Blue.** *Titanic Acid.* **Blue.** *Tungstic Acid.* **Blue, then Green and Blackish-Brown.** *Molybdic Acid.* **Blue, then Muddy or Brown.** *Tantalic*, *Niobic*, and *Pelopic Acid.* **Green.** *Chromic Acid.*

Note. — In these tables the terms *oxide, chloride, sulphide,* etc., designate the *proto*-compounds, (compounds containing 1 eq. of metal and one of non-metallic substance) whilst other combinations are distinguished by prefixes, except in those cases where in the original text the terms were used in a general sense. — Trans.

TABLE II.
TESTING.

II. BEHAVIOR OF METALLIC OXIDES BEFORE THE BLOWPIPE WITH PHOSPHATE OF AMMONIA-SODA AND BORAX.

We saturate the bead (found upon the coil of the platinum wire, or, in experiments with the reducing flame, also upon charcoal), gradually with the finely powdered substance. The colors of the beads differ greatly, according to the temperature of the globules and also to the quantity of the dissolved oxide. (The following abbreviations are h. hot, c. cold, h. c. hot and cold, f. s. feebly saturated, s. s. strongly saturated.

COLOR OF THE BEADS.	With Phosphate of Ammonia-soda.		With Borax.	
	In the Oxidizing Flame.	*In the Reducing Flame.*	*In the Oxidizing Flame.*	*In the Reducing Flame.*
COLORLESS: —	*Silica* gives skeleton of silica. *Alumina. Oxide of tin.* — h. c. all *alkaline earths* and *earths* (s. s. not clear). *Tantalic, niobic, pelopic, titanic,* and *tungstic acid. Oxide of zinc,* of *cadmium, teroxide of bismuth, oxide of lead, teroxide of antimony* (f. s.); s. s. yellowish.	*Silica* gives skeleton of silica, *Alumina.* All *alkaline earths* and *earths* (s.s. not clear) *ses. ox. of cerium, oxide of didymium, ses. ox. of manganese, oxide of tin.*	h. c. *Silica, alumina, oxide of tin.* h. c. (s. s. not clear): all *alkaline earths* and *earths, oxide of silver, tantalic, niobic, pelopic, tellurous acid.* f. s. *Titanic, tungstic, molybdic acid, oxide of zinc,* of *cadmium,* of *lead, teroxide* of *bismuth* and of *antimony.*	h. c. *Silica, alumini, oxide of tin.* h. c. (s. s. not clear): all *alkaline earths* and *earths, oxide of lanthanum, ses. ox. of cerium, tantalic acid.* h. c. *Ses. ox. of manganese,* of *didymium.* h. *Oxide of copper.*
YELLOW: — (to brown).	h. (s. s.) *Sesquioxide of iron,* of *cerium.* h. *Vanadic acid, ses. ox. of uranium, oxide of silver.* c. *Oxide of nickel.*	h. *Sesquioxide of iron* (yellow to red), *titanic acid.*	h. *Ses. ox. of iron,* of *uranium* (f. s.). h. *Vanadic acid.* h. *Oxide of lead, teroxide of bismuth,* of *antimony* (s. s.).	h. *Tungstic acid.* (h. *Titanic, vanadic,* and *molybdic acid,* yellow to brown.)
RED: —	h. (s. s.) *Ses. ox. of iron,* of *cerium.* h. *Oxide of nickel, ses. ox. of chromium.*	h. *Sesquioxide of iron.* c. *Titanic* and *tungstic acid* containing iron (blood-red).	h. *Sesquioxide of cerium,* of *iron.* c. *Oxide of nickel* (reddish-brown).	c. *Oxide of copper* (opaque s. s.).
VIOLET: — (Amethyst).	h. *Ses. ox. of manganese, oxide of didymium.*	c. *Titanic acid, niobic acid* (s. s.).	h. c. *Sesquioxide of manganese, oxide of didymium, oxide of nickel* containing cobalt.	
BLUE: —	h. *Oxide of cobalt.* c. *Oxide of copper.*	h. c. *Oxide of cobalt.* h. *Tungstic acid, niobic acid* (s. s.).	h. c. *Oxide of cobalt;* c. *Oxide of copper.*	h. c. *Oxide of cobalt.*
GREEN: —	h. *Oxide of copper, molybdic acid.* c. *Sesquioxide of chromium,* and of *uranium.* h. *Ses. ox. of iron* containing *cobalt* or *copper.*	c. *Sesquioxide of chromium,* of *uranium, vanadic acid, molybdic acid.*	c. *Ses. ox. of chromium, vanadic acid.* h. *Oxide of copper, ses. ox. of iron,* containing cobalt and copper.	h. c. *Sesquioxide of iron,* of *uranium,* of *chromium.* c. *Vanadic acid.*
GRAY: — (dull).		c. *Oxide of silver,* of *zinc,* of *cadmium,* of *lead, teroxide of bismuth,* and of *antimony. Tellurous acid, oxide of nickel.*		As with phosphate of ammonia-soda. — Also *niobic* or *pelopic acid* (s. s.).

TABLE III.
Aufschliessung, G.

III. CONVERSION OF INSOLUBLE COMPOUNDS INTO SOLUBLE.

If a finely pulverized compound, after being repeatedly treated either with *water*, or with *dilute* or *concentrated chlorhydric acid, nitric acid,* or *aqua regia,* is insoluble, or is not decomposed or attacked by the acids in such a way as to afford decisive conclusions as to the nature of the insoluble compound, then the latter must be *made soluble* in order that its constituents may be determined in the humid way. Since the process in many cases depends upon the result of the preliminary examination, the latter should be conducted with great care. If no *decisive* indication for the treatment of the insoluble compound according to this table be given, then it is always to be fused in form of a fine powder with four parts of carbonate of soda-potassa, and the fused mass treated with water, the washed residue with chlorhydric acid. Platinum crucibles should never be employed for fusion of substances containing *arsenic* or any *easily reducible* metal (antimony, tin, lead, bismuth, etc.).

a. Sulphates. (*Sulphate of baryta, of strontia, and of lead.*)	**b. Silicic Acid and Silicates.**	**c. Fluorides.** (*Fluorspar, etc.*)	**d. Alumina or Aluminates.**	**e. Ses. Oxide of Chromium.** (*Chromic Iron.*)
With soda upon charcoal they give *Hepar.* *Sulphate of baryta* and of *strontia* are decomposed by fusing with 4 parts carbonated alkali. After treatment with water and washing, the solution contains the *acid,* the residue the *base* (now soluble in chlorhydric acid). *Sulphate of lead* gives with soda a metallic grain, is blackened with sulphide of ammonium, and is dissolved in basic tartrate of ammonium. *Gypsum* is somewhat soluble in water.	Give with phosphate of ammonia-soda *skeleton of silica.* The solution of decomposable silicates is effected through chlorhydric acid. That of the undecomposable, by fusion with 3—4 parts carbonated alkali (or hydrate of baryta), and treatment with *chlorhydric acid.* The silicic acid is separated by evaporating with free chlorhydric acid, or by fluohydric acid (see p. 162).	With concentrated sulphuric acid they give *fluohydric acid gas,* which etches glass. The solubility is effected by fusing with 4 parts carbonated alkali (completely by addition of silica) and boiling with water. The solution contains the *acids,* the washed residue the *base;* (now soluble in chlorhydric acid).	When ignited with solution of cobalt they give a *blue* infusible mass. The solubility is effected by fusing with 3—4 parts bisulphate (or also carbonate) of alkali and treating with water or chlorhydric acid (see p. 16).	Gives with phosphate of ammonia-soda and borax green beads in the outer and inner flame. The solubility is effected by fusing with bisulphate of potassa, or carbonated alkali and nitre. Chromic iron requires successive treatment by both methods. (see p. 24).

f. Oxide of Tin or Antimonic Acid.	**g. Titanic, Tungstic, Niobic, Pelopic or Tantalic Acid.**	**h. Chlorides** (*Chloride, Bromide, Iodide of Silver*). **Sulphides** (*Sulphide of Molybdenum, etc.*).	**i. Reguline Metals.** (*Irid-osmium,* or residue of platinum ores).	**k. Carbon.**
With soda upon charcoal they give ductile or brittle metallic grains and are colored by sulphide of ammonium. By fusion with 3—4 parts carbonated alkali they become soluble in acids. — They are also soluble in excess of yellow sulphide of ammonium.	With phosphate of ammonia-soda they give a *blue, violet,* or (those containing iron) *blood-red* bead, and with zinc and chlorhydric acid a coloring. The solubility is effected by fusing with 6 parts bisulphate (or also carbonate) of alkali (see pp. 20, 22, and 99).	*Chloride, bromide,* and *iodide of silver* give with soda a silver granule. — The solubility is effected by means of zinc and dilute sulphuric acid, or by fusing with lime or carbonated alkali, the metal being separated. — *Lead-glance* gives a metallic granule, and with nitric acid, sulphate of lead. (*a*). *Sulphide of molybdenum* gives, with phosphate of ammonia-soda, yellowish-green beads, and is changed by roasting into molybdic acid, becoming blue with zinc and chlorhydric acid.	The insoluble mass has metallic lustre or is black, pulverulent, and not changeable by heat. The solubility is effected by igniting the powder mixed with common salt in chlorine gas, or with hydrate of potassa and chlorate of potassa (see p. 96).	The insoluble mass is black (the diamond colorless) and disappears when subjected to great heat in an open platinum crucible or before the blowpipe. It deflagrates when fused with nitre, carbonate of potassa being formed, and when ignited with oxide of copper, gives carbonic acid.

IV, COMPORTMENT OF THE SOLUTIONS OF METALLIC OXIDES WITH CHLORHYDRIC ACID, SULPHYDRIC ACID, SULPHIDE OF AMMONIUM, AND CARBONATE OF AMMONIA, USED SUCCESSIVELY.

Chlorhydric Acid.	**Sulphydric Acid.** †			NH_2 + **Sulphide of Ammonium.**			**Carbonate of Ammonia.**	
Oxides which are precipitated as *chlorides* from a neutral or acid solution by *chlorhydric acid.**	*Oxides* which are partially *reduced* in an acid solution whilst *sulphur* is precipitated.*	*Oxides which are precipitated by sulphydric acid from their solutions, acidulated by chlorhydric or nitric acid. — The sulphides are: —*		*Oxides which are precipitated from neutral solutions, by sulphide of ammonium (in the presence of chloride of ammonium).*			Oxides which are precipitated neither by sulphide of ammonium nor by sulphydric acid. By carbonate of ammonia, in the presence of chloride of ammonium are	
		Soluble in Sulphide of Ammonium.	*Insoluble in Sulphide of Ammonium.*	*As Sulphides.**	*As Oxides:* also precipitable by ammonia.	*As Salts:* ‡ also precipitable by ammonia.	*precipitated:**	*not precipitated:*
Oxide of lead, white, crystallizable; soluble in much water, precipitable by sulphuric acid. Oxide of silver, white, curdy; soluble in ammonia, whence it is precipitable by nitric acid. Suboxide of mercury, white, pulverulent, is blackened by ammonia.	Sesquioxide of iron, the fluid is decolorized and contains oxide. Chromic acid, the fluid becomes green and contains oxide.	Teroxide of antimony, Antimonic acid, } orange. Arsenious acid, Arsenic acid, } yellow. Oxide of tin, brown. Binoxide of tin, yellow. Teroxide of gold, Binoxide of platinum, [Binoxide of iridium], } blackish brown. [Binoxide of Molybdenum], brown. [Selenious acid], reddish yellow. [Tellurium acids], black.	Suboxide of mercury, Oxide of mercury,‡ Oxide of silver, " " lead, " " copper, } black. " " cadmium, yellow. Teroxide of bismuth, brown. [Oxides of palladium], [Oxides of osmium], [Oxides of rhodium], [Oxides of ruthenium], } black or brown.	Oxide of nickel, " " cobalt, " " iron, Ses. ox. of iron, } black. Oxide of uranium, Sesquioxide of uranium, } blackish brown. Oxide of manganese, flesh-red. Oxide of zinc, white.	*a. Soluble in Potassa.* Alumina, [Glucina], } colorless. Sesquioxide of chromium, green. [Tantalic acid],† [Niobic acid], [Pelopic acid]. *b. Insoluble in Potassa.* [Oxide of cerium], [" " lanthanum], [Oxide of didymium]. [Yttria], [Oxide of erbium], [" " terbium], [Zerconia], [Thoria], [Titanic acid], } mostly colorless or white.	*a. In presence of Phosphoric Acid.* Magnesia, crystalline. *b. In the presence of Phosphoric or Oxalic Acid.* Lime, Strontia, Baryta, } white.	white. Baryta, Strontia, Lime.	*a. Precipitable by Phosphate of Soda.* Magnesia, crystalline. *b. Not precipitable by Phosphate of Soda.* Potassa, Soda, [Lithia], Ammonia.
* In an *alkaline* solution chlorhydric acid (and also nitric acid) may cause a precipitate when any of the following are present: — *Silicic acid,* *Boracic acid,* *Antimonic acid,* *Tungstic acid,* *Molybdic acid,* farther, *oxides* soluble in alkalies (*ox. of lead, alumina,* in excess, soluble in nitric acid) as well as *cyanides* and *ferrocyanides* of *metals*, and all *metallic sulphides* soluble in sulphide of ammonium. A precipitate of sulphur may also be formed in soluble polysulphides and in dithionites.	* A precipitation of sulphur may also be effected by the presence of free chlorine, bromine, iodine; sulphurous nitrous, hypochlorous, chloric, bromic, or iodic acid, etc.	† The oxides of tungsten and of vanadium are precipitated as sulphides only when their solution, mixed with sulphide of ammonium is decomposed by an acid. — The solution of sulphide of tin, $Sn\,S$, in sulphide of ammonium is precipitated by acids, yellow, as $Sn\,S^2$.	‡ The oxide of mercury is precipitated white or yellowish by a little sulphydric acid, by an excess of the acid, black.	* Sulphide of zinc is insoluble in acetic acid, sulphide of cobalt and of nickel are with difficulty soluble in dilute chlorhydric acid and in acetic acid; sulphide of nickel is slightly soluble in yellow sulphide of ammonium (containing ammonia) with a brown color.	† Soluble after being fused with hydrate of potassa.	‡ All these salts are insoluble in potassa, the phosphates of the alkaline earths are soluble in acetic acid, the oxalate of lime is insoluble in acetic acid.	* The precipitation is more complete in the presence of ammonia.	

V. TREATMENT OF A PRECIPITATE FORMED BY SULPHYDRIC ACID, IN WARM ACID SOLUTION.

A portion of the washed precipitate is digested with sulphide of ammonium (with sulphide of potassium if copper be present), filtered if there be a residuum, and to the liquid, dilute sulphuric acid is added. (If the solution be partial, the remaining portion of the precipitate is subjected to the same treatment.) If the precipitate formed by dilute sulphuric acid be not *white, milky*, (of sulphur alone) but *flocculent* and more or less colored, then we proceed with it according to A. — The precipitate, insoluble in sulphide of ammonium, is examined according to B.

A. The Portion soluble in Sulphide of Ammonium.

<table>
<tr><td colspan="2">The precipitate is <i>yellow</i> (arsenic, tin) or <i>orange</i> (antimony).
<i>Digestion with sesquicarbonate of ammonia.</i></td><td colspan="2">The precipitate is <i>dark</i> colored.</td></tr>
<tr><td><i>Solution contains:</i> —
<i>Sulphide of arsenic</i> (a little of sulphide of tin).
Precipitate with dilute chlorhydric acid, dissolve the precipitate in chlorhydric acid and a little chlorate of potassa, and test the solution in Marsh's apparatus (page xxxi.). (Arsenic spots disappear in hypochlorite of soda.)
— Or, according to page 86, by reduction with soda and cyanide of potassium; by this tin yields ductile metallic scales.</td><td><i>Residue contains:</i> —
<i>Sulphide of antimony, sulphide of tin.</i>
Dissolve in chlorhydric acid and a little chlorate of potassa, add metallic zinc to the solution in a test tube serving as Marsh's apparatus, and test the gas for <i>antimony</i>; if the spots do not disappear in hypochlorite of soda, the black metallic powder found (with metallic zinc) in the tube after evolution of gas has ceased, is rinsed down, thoroughly washed, and warmed with chlorhydric acid. With chloride of mercury in presence of tin (page 60) the solution gives a gray or white precipitate.
Or a mixture of arsenietted and antimonietted hydrogen (page 81) is tested by being conducted into nitric acid.</td><td><i>It may contain:</i> —
<i>Sulphide of copper</i> (traces),
" " <i>platinum,</i>
" " <i>iridium,</i>
" " <i>gold,</i>
" " <i>tellurium,</i>
" " <i>selenium,</i>
" " <i>molybdenum,</i>
" " <i>tungsten,</i>
" " <i>vanadium.</i></td><td>Are recognized by their behavior towards reagents (chloride of tin, sulphurous acid, etc.), as well as by testing with the blowpipe.</td></tr>
</table>

B. The Portion insoluble in Sulphide of Ammonium.

The well-washed precipitate is treated, by aid of heat, with concentrated *nitric acid* (free from chlorine). It is either *fully dissolved*, or there is a *residue*. (If the original fluid [before precipitation by sulphydric acid] was acidulated with chlorhydric acid, then this precipitate can contain no sulphide of silver, and no sulphide of mercury arising from the suboxide, though it might from the oxide.)
Osmium, rhodium, and ruthenium, are to be sought for only in the investigation of platinum ore.

<table>
<tr><td colspan="3"><i>Residue may consist of:</i> —</td></tr>
<tr><td><i>Sulphur.</i>
Yellow or gray balls, often inclosing metallic sulphides.</td><td><i>Sulphide of mercury.</i>
Black, flaky. — The solution in aqua-regia is precipitated by chloride of tin.</td><td><i>Sulphate of lead.</i>
White, pulverulent, soluble in basic tartrate of ammonia.</td></tr>
<tr><td colspan="3">If sulphide of mercury is found, the original fluid is tested for the <i>oxide</i> and <i>suboxide</i> of <i>mercury</i>. <i>Chlorhydric acid is added to the fluid.</i></td></tr>
</table>

<table>
<tr><td><i>Precipitate.</i>
Subchloride of mercury.
Becomes black with ammonia or potassa.</td><td><i>Filtrate.</i>
Chloride of mercury.
Excess of chloride of tin precipitates metallic mercury; recognized by rubbing on clean copper.</td></tr>
</table>

<table>
<tr><td colspan="6"><i>Solution may contain:</i> —Oxide of lead, of silver, teroxide of bismuth, oxide of copper, cadmium, and of palladium.
<i>Dilute sulphuric acid is added to it.</i></td></tr>
<tr><td rowspan="4"><i>Precipitate.</i>
Sulphate of lead.
Soluble in basic tartrate of ammonia, thence it is precipitated by chromate of potassa.</td><td colspan="5"><i>Chlorhydric acid is added to the filtrate:</i> —</td></tr>
<tr><td rowspan="3"><i>Precipitate.</i>
Chloride of silver.
Soluble in ammonia, thence it is precipitated by nitric acid.</td><td colspan="4"><i>The filtrate is supersaturated with ammonia:</i> —</td></tr>
<tr><td rowspan="2"><i>Precipitate.</i>
Teroxide of bismuth.
Its solution in a little chlorhydric acid becomes turbid with water.</td><td colspan="3"><i>The filtrate may contain:</i> —</td></tr>
<tr><td>Oxide of copper.
The blue ammoniacal solution is (after acidulation) precipitated reddish brown by ferrocyanide of potassium.</td><td>Oxide of cadmium.
The colorless ammoniacal solution is precipitated <i>yellow</i> by sulphydric acid.</td><td>Oxide of palladium.
The original (<i>brown</i>) fluid is precipitated black by iodide of potassium.</td></tr>
<tr><td colspan="6">For the recognition of oxide of cadmium in presence of oxide of copper, cyanide of potassium is added to the blue ammoniacal solution, until the color vanishes, then only cadmium is precipitated by sulphydric acid.</td></tr>
</table>

TABLE VI.
EXAMINATION OF METALLIC OXIDES.

VI. TREATMENT OF THE PRECIPITATE FORMED BY SULPHIDE OF AMMONIUM, IN THE PRESENCE OF CHLORIDE OF AMMONIUM.

If *nickel* is present the filtrate is brown. *After being washed* the precipitate is treated upon the filter with warm dilute chlorhydric acid. If there is a *black* residue (of sulphide of cobalt or of nickel) it is tested by the blowpipe for cobalt. The precipitate is now completely dissolved in (not too much) hot chlorhydric acid, with the addition of some nitric acid (or chlorate of potassa). — (If but *one* base is to be sought for, the original fluid may also be employed for testing according to this table. It may serve also for determining, when iron is present, whether it appears as oxide or as sesquioxide.)

The Solution is supersaturated with Caustic Potassa, the Precipitate, if one remain, gently digested and filtered.

The *Fluid* or *Filtrate* may contain: * —

Sesquioxide of chromium, oxide of zinc, alumina, glucina.
Long boiling of the (green) potassa solution: —

Precipitate:

Sesquioxide of chromium.
(Also glucina and oxide of zinc.)
Testing by the blowpipe.

Filtrate may contain: —

Oxide of zinc,
Alumina,
Glucina.

Separate the filtrate into two portions and add: —

To one part,
Sulphydric acid.

Precipitate:

Sulphide of zinc.

To the other, — a sufficient quantity of *chlorhydric acid* and then *carbonate of ammonia.*

Precipitate:

Alumina, glucina.
Testing by the blowpipe.
(Glucina is soluble in carbonate of ammonia).

* To detect small quantities of *alumina* along with sesquioxide of iron, the precipitate by sulphide of ammonium is boiled with potassa, the filtrate saturated with chlorhydric acid, and the clear fluid neutralized with carbonate of ammonia. *Ses. ox. of chromium* and of *iron* are successively precipitated according to their relative quantity (p. 47). From a solution containing magnesia along with alumina (or ses. ox. of chromium), a part of the *magnesia* is always precipitated by ammonia (or sulphide of ammonium), with the other oxides, as a gelatinous compound insoluble in potassa. They are separated by dissolving repeatedly in chlorhydric acid and precipitating with ammonia, in presence of much *chloride of ammonium.* The separation of *sesquioxide of chromium* from alumina, magnesia, and ses. ox. of iron is more perfectly effected by fusion with carbonated alkali and nitre. — For separation of alumina from phosphorus see p. 123.

The *Precipitate* may contain: —

Oxide of cobalt, nickel, and of manganese, ses. ox. of iron and of uranium, phosphate of baryta, strontia, lime, and of magnesia, oxalate of lime (fluoride of calcium), all rare earths, insoluble in potassa. — (Also alumina and ses. ox. of chromium with magnesia; oxide of zinc with ses. ox. of iron (see note).
Dissolve the washed precipitate in a little chlorhydric acid, add chloride of ammonium and ammonia.

Filtrate may contain: — *

Oxide of cobalt, nickel, and of manganese (oxide of zinc, magnesia).
Precipitate the fluid (slightly acidulated with acetic acid) with sulphydric acid, *by aid of heat.*

Precipitate:

Sulphide of cobalt,
" " nickel,
(Sulphide of zinc).

Test for cobalt by the blowpipe; for nickel with *chlorine water* in the solution (p. 36) heated with excess of cyanide of potassium, and then mixed with caustic potassa and *cooled.*

Filtrate:

Oxide of manganese.
(magnesia)

Evaporate to dryness and test the residue by fusing with soda and nitre upon platinum foil. A bluish green mass indicates manganese. Or we test the original substance with binoxide of lead and nitric acid (p. 39).

* The separation of oxide of zinc from ses. ox. of iron by means of potassa is not complete, since by the presence of the latter, some oxide of zinc always goes over into the ammoniacal fluid and is found as sulphide of zinc. *Ses. ox. of iron* is separated more exactly (and the presence of small quantities detected more perfectly) from oxide of zinc, as well as from oxide of manganese, nickel, and of cobalt, by boiling the *weakly acid* solution, after adding acetate of soda; thus all the iron is precipitated, if it be present as the ses. oxide.

Precipitate may contain: —

Ses. ox. of iron, uranium, phosphate of baryta, strontia, lime, and of magnesia, oxalate of lime, fluoride of calcium, all the rare earths (also alumina and ses. ox. of chromium).
Digest the precipitate with concentrated solution of carbonate of ammonia.†

Residue may contain: —

Ses. ox. of iron, phosphate of baryta, strontia, lime, and of magnesia, oxalate of lime, (fluoride of calcium).
Dissolve in a little chlorhydric acid and test the solution in separate portions: —

a. For *ses. ox. of iron* (with ferrocyanide of potassium).
b. For *baryta* and *strontia* (with solution of gypsum).
c. For *lime* (with oxalate of potassa and acetate of soda).
d. For *magnesia* (add acetate of soda, then ses. chloride of iron until reddish color is produced, heat to boiling, precipitate the filtrate with carbonate of ammonia and test with phosphate of soda).
e. For *phosphoric acid* (add, *whilst cold,* acetate of soda, then a few drops of ses. chloride of iron, or molybdate of ammonia).
f. For *oxalic acid* (oxalate of lime is precipitated white by acetate of soda; the precipitate is insoluble in acetic acid, and is changed by ignition into carbonate of lime).*
g. For *fluorine* (with the original substance, according to p. 154).

* Also phosphate of ses. ox. of iron is, *when cold,* precipitated from the chlorhydric acid solution (made as neutral as possible) by acetate of soda. (Yellowish, flocculent, or gelatinous.)

Solution may contain: —

Ses. ox. of uranium,*
Oxide of cerium, **
" " lanthanum, **
" " didymium, **
Yttria, **
Thorina, **
Zirconia. **

* When supersaturated with chlorhydric acid the solution gives, with ferrocyanide of potassium, in the presence of ses. ox. of uranium, a brown precipitate.

** They almost all form with sulphate of potassa, double salts difficultly soluble. (p. 19.)

† Digestion with carbonate of ammonia is only employed when there is reason to suppose rare oxides to be present.

VII. A PRECIPITATE BY CARBONATE OF AMMONIA, IN PRESENCE OF CHLORIDE OF AMMONIUM AND FREE AMMONIA.

Carbonate of Baryta, of Strontia, and of Zinc, or a mixture of them.

The washed precipitate is dissolved upon the filter with a little chlorhydric acid, and the solution divided into three portions. If only *one* base is to be sought, the original solution can also be employed for that purpose.

I. Portion.	**II. Portion.**	**III. Portion.**	**Remarks.**
Addition of *sulphate of lime.* Immediate precipitation: — Baryta. Becomes turbid after short time: — Strontia. The fluid remains clear: — Lime.	Precipitate with excess of dilute sulphuric acid,* supersaturate the filtrate with ammonia, and add oxalate of potassa. Precipitate is insoluble in acetic acid. Lime. * In the absence of baryta and strontia the precipitation by sulphuric acid is unnecessary.	*a. When baryta is present.* Evaporate to dryness, digest the residue with alcohol, and ignite the filtrate. Crimson flame: — Strontia. *b. When baryta is absent.* We recognize strontia more certainly since the solution in chlorhydric acid, by the addition of a solution of sulphate of strontia, does not become turbid even after a long time, whilst sulphate of lime gives a precipitate in a short time.	If there be present *no* metallic oxide precipitable by *sulphydric acid* or *sulphide of ammonium*, the original solution may also be used for this investigation (with exception of Portion III. *a*), unless the presence of magnesia or alkalies prevents the result being exact. *Baryta* is recognized with more certainty in the presence of strontia and lime, by means of a solution of sulphate of strontia, which causes a white precipitate, appearing, after a short time, when only traces of baryta are present. The *separation* of baryta from strontia is accomplished by silicofluohydric acid, with the addition of alcohol in which the silicofluoride of barium is quite insoluble.

VIII. A FLUID WHICH IS PRECIPITATED NEITHER BY SULPHYDRIC ACID, SULPHIDE OF AMMONIUM, NOR BY CARBONATE OF AMMONIA.

It may contain: — *Magnesia, Potassa, Soda, Lithia, Ammonia,* or *a mixture* of these bases.

Evaporate a portion (not too small) of the fluid upon platinum foil; if after ignition there is no residuum, neither magnesia nor alkalies need be considered, but ammonia should be.

Test for Ammonia.	**Test for Magnesia.**	**Test for Potassa, Soda, and Lithia.**
Warm the *original substance* or its solution (*not* the fluid, VIII.) with *much hydrate of potassa.* The presence of *Ammonia* is recognized by the odor, as well as by the white cloud which arises when a glass rod moistened with chlorhydric acid is brought near.	*Phosphate of soda* (and free ammonia if it be not already present) is added to *a portion* of the fluid, VIII. (or to the original solution if it contain no metallic oxides or alkaline earths). The presence of *magnesia* may be recognized by a crystalline precipitate, which is formed slowly when only traces of magnesia are present.	*a. When magnesia is absent.* Evaporate a portion of fluid, VIII. (to which no phosphate of soda has been added) to dryness, apply heat for the removal of the ammoniacal salts, and test the residue before the blowpipe upon platinum wire, or by overflowing with alcohol and ignition. A *violet flame* indicates *potassa* only, a *crimson, lithia,* a *yellow, soda,* or a mixture of soda with potassa or lithia. In the latter case, test the residue for *potassa* by tartaric acid or chloride of platinum and alcohol in solution not too dilute: for *lithia* by boiling with carbonate of potassa and phosphate of soda, whereby a salt forms, soluble with difficulty; or by a mixture of anhydrous ether and alcohol, in which chloride of lithium dissolves. *b. When magnesia is present.* Evaporate to dryness, heat the residue to remove the ammoniacal salts, and warm with water. Add to the solution baryta-water until alkaline reaction ensues, boil and filter. Remove the excess of baryta by ammonia and carbonate of ammonia (or dilute sulphuric acid), and evaporate the filtrate to dryness. If there is a residue, proceed with it as in *a*. Or we test for alkalies according to page 12.

IX. BEHAVIOR OF THE MORE IMPORTANT ACIDS, OR OF THE HALOGENS, BY HEATING THEIR COMPOUNDS WITH CONCENTRATED SULPHURIC ACID.

A quantity of the dry compound is taken upon the point of a small knife, placed in a test tube and overflowed with 3–4 times its volume of concentrated sulphuric acid, then heated, but not to the boiling point of sulphuric acid. With all acids volatile when alone, or which suffer decomposition by sulphuric acid in a higher temperature, the evolution may be observed, of vapor or of gases from whose properties, in most cases, the nature of the acids or of the halogens may be learned.

Non-Volatile Acids.	**Acids Volatile, or Decomposable with Evolution of Volatile Products.**			
		Those evolving vapor or gas are colorless.		
No gas or vapor is evolved. The compound does not blacken by exposure to heat.	*A colored gas is evolved. The compound does not blacken by exposure to heat.*	*The compound does not blacken by ignition.*	*The compound is decomposed by ignition.*	
			Mostly without separation of carbon.	With separation of carbon.
Silicic Acid, recognized by means of phosphate of ammonia-soda before the blowpipe. **Boracic Acid**, after addition of sulphuric acid, it colors the flame of alcohol green. **Phosphoric Acid**, precipitable in neutral solution by sulphate of magnesia, chloride of ammonium, and ammonia; in acid solution by ses. chloride of iron and ac. of soda. **Arsenic Acid**, like the preceding, but the compound gives with soda upon charcoal arsenical odor. **Sulphuric Acid**, the compound gives hepar when heated with soda upon charcoal. **Selenic Acid**, like the preceding. The baryta salt is decomposed by boiling with concentrated chlorhydric acid. **Tungstic Acid**, recognized by testing with blowpipe; becomes blue with zinc and chlorhydric acid. **Molybdic Acid**, recognized by testing with blowpipe, becomes first blue, then brown with zinc and chlorhydric acid. **Titanic Acid**, recognized by testing with the blowpipe; becomes violet with zinc and chlorhydric acid. **Iodic Acid.** The violet vapors of iodine form on addition of sulphate of iron. The compound deflagrates upon charcoal.	**Iodhydric Acid**, the violet vapor colors starch blue. **Bromhydric Acid**, the brown vapor colors starch a fiery yellow. **Bromic Acid.** Like the preceding, the salt deflagrates upon charcoal. **Chloric Acid**, the greenish yellow gas readily explodes, the compound deflagrates upon charcoal. **Hypochlorous Acid**, yellowish green chlorine gas, like the preceding, discoloring solution of indigo. **Nitrous Acid**, red fumes, even with dilute sulphuric or nitric acid. **Nitric Acid**, nearly colorless, acid fumes, which are red if chlorine be present; deeper red if sulphate of iron be added.	**Carbonic Acid**, colorless, makes lime water turbid. **Cyanic Acid**, excites tears, and makes lime water turbid. **Sulphurous Acid**, recognized by its odor; colors dissolved chromate of potassa green. **Sulphydric Acid**, recognized by its odor; colors lead-paper brown. **Chlorhydric Acid**, fumes copiously and precipitates a solution of silver on a glass rod curdy. **Fluohydric Acid**, fumes copiously, etches glass and does not make a solution of silver turbid. **Silicofluohydric Acid**, like the preceding; the gas gives with water a precipitate of silica. **Nitric Acid**, nearly colorless fumes which become red upon addition of sulphate of iron or copper filings.	**Oxalic Acid**, develops carbonic acid and oxide of carbon; the lime salt is insoluble in acetic acid. **Formic Acid**, evolves only combustible carbonic oxide gas. **Cyanhydric Acid**, like the preceding, but evolves cyanhydric acid. **Ferrocyanhydric Acid**, like the preceding; the soluble compound is precipitated blue by the *salts of ses. ox. of iron.* **Ferricyanhydric Acid**, like the preceding; the soluble compound is precipitated blue by the *salts of the oxide of iron.* **Chromic Acid**, evolves oxygen and the flame becomes brown or green. Gives a green bead with phosphate of ammonia-soda. **Dithionous Acid,** **Trithionic** " **Tetrathionic** " **Pentathionic** " } develop sulphurous acid with separation of sulphur.	*a. Acids not volatile per se.* All combinations of these acids are decomposed by sulphuric acid, and blacken, whilst they develop CO_2, CO and SO_2. **Tartaric Acid**, the acid salt of potassa is soluble with difficulty, the lime salt is soluble in caustic potassa. **Racemic Acid**; the lime salt is insoluble in chloride of ammonium. **Citric Acid**; gives a precipitate with excess of lime water only on boiling. **Malic Acid**, is not precipitated by lime water, either warm or cold. **Tannic Acid**, gives a white, viscous precipitate with glue, a blue-black with salts of ses. ox. of iron, ferric oxide. **Gallic Acid**, not precipitable by glue; salts of ferroso-ferric oxide produce a black precipitate. **Uric Acid**, gives a red color with ammonia after evaporation with nitric acid. *b. Acids volatile per se.* The substance does not blacken, or but slightly, with sulphuric acid. **Acetic Acid**, gives with sulphuric acid and alcohol acetic ether; with oxide of lead a salt having alkaline reaction. **Benzoic Acid,** **Succinic** " } Their neutral salts are precipitated a light brown by ses. chloride of iron.

Note. — If by the above methods a hydracide is found, the dry compound contains the corresponding halogen combined with a metal. In a mixture of salts other reactions take place; thus a metallic chloride along with a nitrate develops chlorine and red vapors; along with a chromate brownish-red fumes of chlorchromic acid, etc. The chlorides of mercury are hardly decomposed by sulphuric acid. Metallic sulphides, with concentrated sulphuric acid, develop freely sulphurous acid.

X. BEHAVIOR OF THE MORE IMPORTANT ACIDS TOWARDS REAGENTS.

A. *Examination of Acids in soluble compounds.* Whether the aqueous solution is *neutral, acid,* or *alkaline,* is to be determined by test-paper. If the acid is to be sought in an ammoniacal solution or one as neutral as possible, it is often necessary to remove the heavy metallic oxides or the earths (according to table IV.) present, by which means the *acids of the metals* are found as well as phosphoric or oxalic acid combined with alkaline earths. The quality of the base often excludes the presence of one or more acids, thus rendering their search unnecessary; generally an acid cannot be present in a *neutral* or *acid* solution which already contains the same metallic oxide that must serve as precipitant for this acid; e. g. none of the *acids of sulphur* detected by baryta can be present in a soluble *baryta-compound;* in a *silver* compound, soluble in acids, can no *chlorine* be found, etc. (For exceptions in alkaline solution, see below, table X.) It is evident that in any compound such acids as are added (for solution or neutralization) need not be sought; in all compounds where the reagent can act as precipitant through its acids (or halogen) the *nitrate* of the salt is used; e. g. in compounds of silver, lead, or suboxide of mercury, nitrate of baryta is used instead of chloride of barium. (See continuation, table XI.)

Are Precipitated by Chlorhydric or Nitric Acid:	**Are Precipitated by Chloride of Barium** (or Nitrate of Baryta):	**Are Precipitated by Chloride of Calcium:**		**Are Precipitated by Sulphate of Magnesia** (or Chloride of Magnesium):
From their soluble combinations, generally showing alkaline reactions.	*From the solution previously acidulated with chlorhydric or nitric acid.*	*Only from neutral solution.* The precipitate is soluble in acetic acid.	*From neutral and from acetic solution.* Precipitate is insoluble in acetic acid.	*In the presence of chloride of ammonium and free ammonia.*
Silicic Acid, gelatinous; in dilute solution only by evaporating the acid fluid; also by carbonate of ammonia. Boracic Acid, crystalline only from concentrated solutions. Colors the alcoholic flame green upon addition of sulphuric acid. Antimonic Acid, white, soluble in tartaric acid. Tungstic Acid, white, by boiling, yellow; with zinc and chlorhydric acid, blue. Molybdic Acid, white, soluble in excess, with zinc and chlorhydric acid, blue. Sulphur, yellowish or white; evolves SO_2 from dithionites, and $H S$ from metallic polysulphides. Also: several *oxides* and *metallic sulphides* soluble in potassa, and *cyanides* or *metallic chlorides* soluble in cyanide of potassium. If the alkaline fluid be saturated with sulphydric acid, all the acids of *the metals* which form metallic sulphides insoluble in acids, are precipitated, after acidulation, as *sulphides.* Of the *organic acids, benzoic, uric,* and *tartaric* acid (the latter as acid *potassa* salt) are precipitated by acids from the alkaline solution.	Sulphuric Acid, white, pulverulent; quite insoluble in water and in acids.—In the presence of too much concentrated free acid chloride of barium or nitrate of baryta is precipitated; soluble in much water. Selenic Acid, like sulphuric. The precipitate, when boiled with concentrated chlorhydric acid evolves chlorine. Silicofluohydric Acid, gelatinous, scarcely visible; is decomposed by concentrated acids.	Phosphoric Acid, white, when freshly precipitated soluble in acetic acid without effervescence. Arsenic Acid, like phosphoric; also easily soluble in chloride of ammonium.—The solution in chlorhydric acid is precipitable by sulphydric acid with the aid of heat. Boracic Acid, white, easily soluble in chloride of ammonium; not precipitated from dilute solution. Turmeric paper dipped in a solution of chlorhydric acid is brown after drying. Carbonic Acid, white, soluble in acids with effervescence. Sulphurous Acid, white, precipitated only from concentrated solutions: with zinc and chlorhydric acid, evolves sulphydric acid. Tartaric Acid, white, soluble in chloride of ammonium and caustic potassa; the potassa solution of the precipitate becomes turbid by boiling. Racemic Acid, like tartaric; the precipitate is insoluble in chloride of ammonium. Citric Acid, white, precipitates only by boiling the fluid supersaturated with lime water or ammonia.	Oxalic Acid, white; the precipitate, after heating with acids, evolves carbonic acid. Fluohydric Acid, gelatinous; the precipitate evolves, with concentrated sulphuric acid, fluohydric acid, which etches glass. Sulphuric Acid, white; not from dilute solutions; completely upon addition of alcohol.	Phosphoric Acid, white, crystalline; soluble in all acids, very slowly if the solution be very dilute. Arsenic Acid, like the preceding. The *acid* solution of the precipitate is precipitated by sulphydric acid, with the aid of heat. Tartaric Acid, white. The precipitate forms slowly and only in concentrated solution; it blackens when highly heated.

Separation of Oxalic, Tartaric, Citric, and Malic Acid.

Chloride of calcium and lime water are added until alkaline reaction ensues.

Fluid contains as salt of lime:—		*Precipitate* contains as salt of lime:—	
Citric Acid,	*Malic Acid.*	*Oxalic Acid,*	*Tartaric Acid.*
Heat to boiling.		Treat with cold potassa lye.	
Precipitate:	*Filtrate:*	*Residue.*	*Filtrate.*
Citrate of Lime.	*Malate of Lime.*	*Oxalate of Lime.*	*Tartrate of Lime.*
Soluble in chloride of copper.	Precipitable, after evaporation, by alcohol.	Insoluble in acetic acid and in chloride of copper; soluble in chlorhydric acid.	By boiling, the alkaline solution is precipitated gelatinous.

XI. BEHAVIOR OF THE MORE IMPORTANT ACIDS TOWARDS REAGENTS AND INDIGO SOLUTION.

B. *Testing for acids in compounds which are insoluble in water and in acids.* — From the preliminary testing (according to tables I., III., and IX.), the nature of the compound and the acids possibly present, must be ascertained. — *Inorganic* compounds (which by igniting alone afford no coal) are finely pulverized and fused along with fourfold weight of *pure* carbonate of soda-potassa and the *aqueous* extract (neutralized by chlorhydric, nitric, or acetic acid) is examined according to tables X. and XI. Insoluble compounds of the heavy metallic oxides may also be decomposed by digestion with sulphide of ammonium, the sulphates of the alkaline earths by boiling with a concentrated solution of carbonate of soda; the filtrate contains the acid. Metallic sulphides afford *sulphuric acid* by treatment with nitric acid, aqua regia, or chlorhydric acid and chlorate of potassa. The salts of organic acids insoluble in water are decomposed by boiling with carbonated alkali; and the salts formed by sesquioxide of iron with volatile organic acids, also by ammonia; the filtrate contains the acids combined with the alkali and is examined according to tables X. and XI.

Acids recognizable by Sesquichloride of Iron.		**Acids Precipitable by Nitrate of Silver.**		**Acids decolorizing Indigo Solution.**
A precipitate is formed.	A color is produced.	Only from *neutral* solution.	Likewise from *acid* solution.	
a. *In the presence of free chlorhydric acid.* Ferrocyanhydric Acid, blue; the precipitate is decomposed by potassa into sesquioxide of iron and ferrocyanide of potassium. b. *In neutral solutions, or those containing only free acetic acid.* (If free chlorhydric acid be present add acetate of soda.) Phosphoric Acid, yellowish white; insoluble in acetic acid, soluble in chlorhydric and in acetate of sesquioxide of iron. Arsenic Acid, in like manner; the original compound gives with soda an aliaceous odor. Tannic Acid, blackish-blue. The original compound is precipitated by glue. c. *Only in neutral solution.* Boracic Acid, yellowish. Turmeric paper dipped in the chlorhydric acid solution is, after drying, brown. Benzoic Acid, light brown. The original concentrated solution is precipitated crystalline by chlorhydric acid. Succinic Acid, in like manner. The concentrated solution of the ammonia salt (obtained by digestion with ammonia of the salt of the ses. ox. of iron) is precipitated by chloride of barium in the presence of alcohol and free ammonia.	a. *In the presence of free chlorhydric acid.* Ferricyanhydric Acid, brownish. Salts of the oxide of iron produce a blue precipitate. Sulphcyanhydric Acid, intense blood-red, not vanishing by much chlorhydric acid, becoming yellow by terchloride of gold. b. *Only in neutral solution.* (The color vanishes on addition of chlorhydric acid.) Acetic Acid, reddish-brown; the original salt warmed with alcohol and sulphydric acid has the odor of acetic ether. Formic Acid, in like manner. The original compound reduces the oxide of silver or of mercury evolving carbonic acid. Sulphurous Acid, in like manner; on boiling, the color vanishes without precipitation. The original compound, upon the addition of chlorhydric acid, has the odor of sulphurous acid. Meconic Acid, blood-red, unchangeable by terchloride of gold. Gallic Acid, black. The original solution is not precipitated by glue.	*The precipitate is soluble in dilute nitric acid.** Phosphoric Acid, (tribasic) yellow; also precipitable by chloride of ammonium, ammonia, and sulphate of magnesia. Arsenic Acid, brownish-red; the original compound is precipitable by $H\,S$. Arsenious Acid, egg-yellow; quite like the preceding. Chromic Acid, red; the original yellow or red compound becomes green by $S\,O_2$. Oxalic Acid, white, insoluble in acetic acid. The lime salt is likewise insoluble in acetic acid. Boracic Acid, white, soluble in acetic acid, green alcohol flame after the addition of sulphuric acid. * All these precipitates are soluble in ammonia. The salts of *pyrophosphoric* and *metaphosphoric acid* precipitate nitrate of silver white; the latter gives, after the addition of acetic acid, a precipitate with albumen.	*The precipitate is insoluble in dilute nitric acid.* Chlorhydric Acid, white, soluble in ammonia and in hyposulphite of soda. Bromhydric Acid, in like manner. The original compound colors ether yellow, after the addition of some chlorine water. Iodhydric Acid, yellow, insoluble in ammonia. The original compound gives, with $N\,O_5$ and starch, blue iodide of starch. Iodic Acid, white soluble in ammonia, precipitable therefrom by $S\,O_2$ as $Ag\,I$. The original compound gives, with acetic acid and starch, blue iodide. Cyanhydric Acid, white, soluble in ammonia and in hyposulphite of soda. The original fluid gives, with salts of ferroso-ferric oxide, potassa, and chlorhydric acid, Berlin blue. Ferrocyanhydric Acid, white, insoluble in ammonia. The original compound gives immediately with salts of sesq. ox. of iron Berlin blue. Sulphcyanhydric Acid, white, soluble with difficulty in ammonia; the original solution becomes with ses. chloride of iron blood-red. Sulphydric Acid, black, insoluble in ammonia; also the salts of lead and of copper give black precipitates.	a. *Alone, without addition of an acid.* Free chlorine and bromine; hypochloric, chlorous, and hypochlorous acid, as well as hypochlorites; and free nitric acid not too dilute. Also alkaline metallic sulphides. b. *On the addition of an acid (chlorhydric or sulphuric and heating).* Chlorates; they leave by ignition metallic chlorides. Nitrates; dark color with sulphate of iron and sulphuric acid. Iodates; the dry compound gives with sulphuric acid and sulphate of iron violet vapor of iodine. Bromates; give with sulphuric acid brown vapor of bromine. c. *By boiling or warming with concentrated chlorhydric acid evolve (bleaching) chlorine:* — All the preceding compounds further: — Chromates, Seleniates, Tellurates, Superoxides, and the Acids of Manganese.

ALPHABETICAL INDEX,

BY THE TRANSLATORS.

END.

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